METHOD STATUS TABLE
SW-846, THIRD EDITION, UPDATES I, II, AND IIA

September 1994

- Use this table as a reference guide to identify the promulgation status of SW-846 methods.
- The methods in this table are listed sequentially by number.
- This table should not be used as a Table of Contents for SW-846. Refer to the Table of Contents found in Final Update II (dated September 1994) for the order in which the methods appear in SW-846.

SW-846 METHOD STATUS TABLE
September 1994

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
0010	--	--	Modified Method 5 Sampling Train	Vol II Chap 10	0010 Rev 0 9/86
0020	--	--	Source Assessment Sampling System (SASS)	Vol II Chap 10	0020 Rev 0 9/86
0030	--	--	Volatile Organic Sampling Train	Vol II Chap 10	0030 Rev 0 9/86
1010	--	--	Pensky-Martens Closed-Cup Method for Determining Ignitability	Vol IC Chap 8 Sec 8.1	1010 Rev 0 9/86
1020	1020A	--	Setaflash Closed-Cup Method for Determining Ignitability	Vol IC Chap 8 Sec 8.1	1020A Rev 1 7/92
1110	--	--	Corrosivity Toward Steel	Vol IC Chap 8 Sec 8.2	1110 Rev 0 9/86
1310	1310A	--	Extraction Procedure (EP) Toxicity Test Method and Structural Integrity Test	Vol IC Chap 8 Sec 8.4	1310A Rev 1 7/92
--	1311	--	Toxicity Characteristic Leaching Procedure	Vol IC Chap 8 Sec 8.4	1311 Rev 0 7/92
--	--	1312	Synthetic Precipitation Leaching Procedure	Vol IC Chap 6	1312 Rev 0 9/94

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
1320	--	--	Multiple Extraction Procedure	Vol IC Chap 6	1320 Rev 0 9/86
1330	1330A	--	Extraction Procedure for Oily Wastes	Vol IC Chap 6	1330A Rev 1 7/92
3005	3005A	--	Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy	Vol IA Chap 3 Sec 3.2	3005A Rev 1 7/92
3010	3010A	--	Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy	Vol IA Chap 3 Sec 3.2	3010A Rev 1 7/92
--	--	3015	Microwave Assisted Acid Digestion of Aqueous Samples and Extracts	Vol IA Chap 3 Sec 3.2	3015 Rev 0 9/94
3020	3020A	--	Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy	Vol IA Chap 3 Sec 3.2	3020A Rev 1 7/92
3040	--	--	Dissolution Procedure for Oils, Greases, or Waxes	Vol IA Chap 3 Sec 3.2	3040 Rev 0 9/86
3050	3050A	--	Acid Digestion of Sediments, Sludges, and Soils	Vol IA Chap 3 Sec 3.2	3050A Rev 1 7/92

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	--	3051	Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils	Vol IA Chap 3 Sec 3.2	3051 Rev 0 9/94
3500	3500A	--	Organic Extraction and Sample Preparation	Vol IB Chap 4 Sec 4.2.1	3500A Rev 1 7/92
3510	3510A	3510B	Separatory Funnel Liquid-Liquid Extraction	Vol IB Chap 4 Sec 4.2.1	3510B Rev 2 9/94
3520	3520A	3520B	Continuous Liquid-Liquid Extraction	Vol IB Chap 4 Sec 4.2.1	3520B Rev 2 9/94
3540	3540A	3540B	Soxhlet Extraction	Vol IB Chap 4 Sec 4.2.1	3540B Rev 2 9/94
--	--	3541	Automated Soxhlet Extraction	Vol IB Chap 4 Sec 4.2.1	3541 Rev 0 9/94
3550	--	3550A	Ultrasonic Extraction	Vol IB Chap 4 Sec 4.2.1	3550A Rev 1 9/94
3580	3580A	--	Waste Dilution	Vol IB Chap 4 Sec 4.2.1	3580A Rev 1 7/92
3600	3600A	3600B	Cleanup	Vol IB Chap 4 Sec 4.2.2	3600B Rev 2 9/94

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
3610	3610A	--	Alumina Column Cleanup	Vol IB Chap 4 Sec 4.2.2	3610A Rev 1 7/92
3611	3611A	--	Alumina Column Cleanup and Separation of Petroleum Wastes	Vol IB Chap 4 Sec 4.2.2	3611A Rev 1 7/92
3620	3620A	--	Florisil Column Cleanup	Vol IB Chap 4 Sec 4.2.2	3620A Rev 1 7/92
3630	3630A	3630B	Silica Gel Cleanup	Vol IB Chap 4 Sec 4.2.2	3630B Rev 2 9/94
3640	--	3640A	Gel-Permeation Cleanup	Vol IB Chap 4 Sec 4.2.2	3640A Rev 1 9/94
3650	3650A	--	Acid-Base Partition Cleanup	Vol IB Chap 4 Sec 4.2.2	3650A Rev 1 7/92
3660	3660A	--	Sulfur Cleanup	Vol IB Chap 4 Sec 4.2.2	3660A Rev 1 7/92
--	--	3665	Sulfuric Acid/Permanganate Cleanup	Vol IB Chap 4 Sec 4.2.2	3665 Rev 0 9/94
3810	--	--	Headspace	Vol IB Chap 4 Sec 4.4	3810 Rev 0 9/86

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
3820	--	--	Hexadecane Extraction and Screening of Purgeable Organics	Vol IB Chap 4 Sec 4.4	3820 Rev 0 9/86
--	--	4010 (Update IIA; dated 8/93)	Screening for Pentachlorophenol by Immunoassay	Vol IB Chap 4 Sec 4.4	4010 Rev 0 8/93
5030	5030A	--	Purge-and-Trap	Vol IB Chap 4 Sec 4.2.1	5030A Rev 1 7/92
5040	--	5040A	Analysis of Sorbent Cartridges from Volatile Organic Sampling Train (VOST): Gas Chromatography/Mass Spectrometry Technique	Vol IB Chap 4 Sec 4.2.1	5040A Rev 1 9/94
--	--	5041	Protocol for Analysis of Sorbent Cartridges from Volatile Organic Sampling Train (VOST): Wide-bore Capillary Column Technique	Vol IB Chap 4 Sec 4.2.1	5041 Rev 0 9/94
--	--	5050	Bomb Preparation Method for Solid Waste	Vol IC Chap 5	5050 Rev 0 9/94
6010	6010A	--	Inductively Coupled Plasma-Atomic Emission Spectroscopy	Vol IA Chap 3 Sec 3.3	6010A Rev 1 7/92

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	--	6020	Inductively Coupled Plasma - Mass Spectrometry	Vol IA Chap 3 Sec 3.3	6020 Rev 0 9/94
7000	7000A	--	Atomic Absorption Methods	Vol IA Chap 3 Sec 3.3	7000A Rev 1 7/92
7020	--	--	Aluminum (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7020 Rev 0 9/86
7040	--	--	Antimony (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7040 Rev 0 9/86
7041	--	--	Antimony (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7041 Rev 0 9/86
7060	--	7060A	Arsenic (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7060A Rev 1 9/94
7061	7061A	--	Arsenic (Atomic Absorption, Gaseous Hydride)	Vol IA Chap 3 Sec 3.3	7061A Rev 1 7/92
--	--	7062	Antimony and Arsenic (Atomic Absorption, Borohydride Reduction)	Vol IA Chap 3 Sec 3.3	7062 Rev 0 9/94
7080	--	7080A	Barium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7080A Rev 1 9/94

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	7081	--	Barium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7081 Rev 0 7/92
7090	--	--	Beryllium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7090 Rev 0 9/86
7091	--	--	Beryllium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7091 Rev 0 9/86
7130	--	--	Cadmium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7130 Rev 0 9/86
7131	--	7131A	Cadmium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7131A Rev 1 9/94
7140	--	--	Calcium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7140 Rev 0 9/86
7190	--	--	Chromium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7190 Rev 0 9/86
7191	--	--	Chromium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7191 Rev 0 9/86
7195	--	--	Chromium, Hexavalent (Coprecipitation)	Vol IA Chap 3 Sec 3.3	7195 Rev 0 9/86

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
7196	7196A	--	Chromium, Hexavalent (Colorimetric)	Vol IA Chap 3 Sec 3.3	7196A Rev 1 7/92
7197	--	--	Chromium, Hexavalent (Chelation/Extraction)	Vol IA Chap 3 Sec 3.3	7197 Rev 0 9/86
7198	--	--	Chromium, Hexavalent (Differential Pulse Polarography)	Vol IA Chap 3 Sec 3.3	7198 Rev 0 9/86
7200	--	--	Cobalt (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7200 Rev 0 9/86
7201	--	--	Cobalt (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7201 Rev 0 9/86
7210	--	--	Copper (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7210 Rev 0 9/86
--	7211	--	Copper (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7211 Rev 0 7/92
7380	--	--	Iron (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7380 Rev 0 9/86
--	7381	--	Iron (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7381 Rev 0 7/92

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
7420	--	--	Lead (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7420 Rev 0 9/86
7421	--	--	Lead (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7421 Rev 0 9/86
--	7430	--	Lithium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7430 Rev 0 7/92
7450	--	--	Magnesium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7450 Rev 0 9/86
7460	--	--	Manganese (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7460 Rev 0 9/86
--	7461	--	Manganese (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7461 Rev 0 7/92
7470	--	7470A	Mercury in Liquid Waste (Manual Cold-Vapor Technique)	Vol IA Chap 3 Sec 3.3	7470A Rev 1 9/94
7471	--	7471A	Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)	Vol IA Chap 3 Sec 3.3	7471A Rev 1 9/94
7480	--	--	Molybdenum (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7480 Rev 0 9/86

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
7481	--	--	Molybdenum (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7481 Rev 0 9/86
7520	--	--	Nickel (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7520 Rev 0 9/86
7550	--	--	Osmium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7550 Rev 0 9/86
7610	--	--	Potassium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7610 Rev 0 9/86
7740	--	--	Selenium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7740 Rev 0 9/86
7741	--	7741A	Selenium (Atomic Absorption, Gaseous Hydride)	Vol IA Chap 3 Sec 3.3	7741A Rev 1 9/94
--	--	7742	Selenium (Atomic Absorption, Borohydride Reduction)	Vol IA Chap 3 Sec 3.3	7742 Rev 0 9/94
7760	7760A	--	Silver (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7760A Rev 1 7/92
--	7761	--	Silver (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7761 Rev 0 7/92

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
7770	--	--	Sodium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7770 Rev 0 9/86
--	7780	--	Strontium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7780 Rev 0 7/92
7840	--	--	Thallium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7840 Rev 0 9/86
7841	--	--	Thallium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7841 Rev 0 9/86
7870	--	--	Tin (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7870 Rev 0 9/86
7910	--	--	Vanadium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7910 Rev 0 9/86
7911	--	--	Vanadium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7911 Rev 0 9/86
7950	--	--	Zinc (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7950 Rev 0 9/86
--	7951	--	Zinc (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7951 Rev 0 7/92

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
8000	8000A	--	Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8000A Rev 1 7/92
8010	8010A	8010B	Halogenated Volatile Organics by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8010B Rev 2 9/94
--	8011	--	1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane by Microextraction and Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8011 Rev 0 7/92
8015	8015A	--	Nonhalogenated Volatile Organics by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8015A Rev 1 7/92
8020	--	8020A	Aromatic Volatile Organics by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8020A Rev 1 9/94
--	8021	8021A	Halogenated Volatiles by Gas Chromatography Using Photoionization and Electrolytic Conductivity Detectors in Series: Capillary Column Technique	Vol IB Chap 4 Sec 4.3.1	8021A Rev 1 9/94
8030	8030A	--	Acrolein and Acrylonitrile by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8030A Rev 1 7/92
--	--	8031	Acrylonitrile by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8031 Rev 0 9/94

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	--	8032	Acrylamide by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8032 Rev 0 9/94
8040	8040A	--	Phenols by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8040A Rev 1 7/92
8060	--	--	Phthalate Esters	Vol IB Chap 4 Sec 4.3.1	8060 Rev 0 9/86
--	--	8061	Phthalate Esters by Capillary Gas Chromatography with Electron Capture Detection (GC/ECD)	Vol IB Chap 4 Sec 4.3.1	8061 Rev 0 9/94
--	8070	--	Nitrosamines by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8070 Rev 0 7/92
8080	--	8080A	Organochlorine Pes-ticides and Polychlorinated Biphenyls by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8080A Rev 1 9/94
--	--	8081	Organochlorine Pesticides and PCBs as Aroclors by Gas Chromatography: Capillary Column Technique	Vol IB Chap 4 Sec 4.3.1	8081 Rev 0 9/94
8090	--	--	Nitroaromatics and Cyclic Ketones	Vol IB Chap 4 Sec 4.3.1	8090 Rev 0 9/86

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
8100	--	--	Polynuclear Aromatic Hydrocarbons	Vol IB Chap 4 Sec 4.3.1	8100 Rev 0 9/86
--	8110	--	Haloethers by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8110 Rev 0 7/92
8120	--	8120A	Chlorinated Hydrocarbons by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8120A Rev 1 9/94
--	--	8121	Chlorinated Hydrocarbons by Gas Chromatography: Capillary Column Technique	Vol IB Chap 4 Sec 4.3.1	8121 Rev 0 9/94
8140	--	--	Organophosphorus Pesticides	Vol IB Chap 4 Sec 4.3.1	8140 Rev 0 9/86
--	8141	8141A	Organophosphorus Compounds by Gas Chromatography: Capillary Column Technique	Vol IB Chap 4 Sec 4.3.1	8141A Rev 1 9/94
8150	8150A	8150B	Chlorinated Herbicides by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8150B Rev 2 9/94
--	--	8151	Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzyl-ation Derivati-zation: Capillary Column Technique	Vol IB Chap 4 Sec 4.3.1	8151 Rev 0 9/94

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
8240	8240A	8240B	Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)	Vol IB Chap 4 Sec 4.3.2	8240B Rev 2 9/94
8250	--	8250A	Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)	Vol IB Chap 4 Sec 4.3.2	8250A Rev 1 9/94
--	8260	8260A	Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique	Vol IB Chap 4 Sec 4.3.2	8260A Rev 1 9/94
8270	8270A	8270B	Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique	Vol IB Chap 4 Sec 4.3.2	8270B Rev 2 9/94
--	--	8275	Thermal Chromatography/Mass Spectrometry (TC/MS) for Screening Semivolatile Organic Compounds	Vol IB Chap 4 Sec 4.4	8275 Rev 0 9/94
8280	--	--	The Analysis of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans	Vol IB Chap 4 Sec 4.3.2	8280 Rev 0 9/86

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	--	8290	Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS)	Vol IB Chap 4 Sec 4.3.2	8290 Rev 0 9/94
8310	--	--	Polynuclear Aromatic Hydrocarbons	Vol IB Chap 4 Sec 4.3.3	8310 Rev 0 9/86
--	--	8315	Determination of Carbonyl Compounds by High Performance Liquid Chromatography (HPLC)	Vol IB Chap 4 Sec 4.3.3	8315 Rev 0 9/94
--	--	8316	Acrylamide, Acrylonitrile and Acrolein by High Performance Liquid Chromatography (HPLC)	Vol IB Chap 4 Sec 4.3.3	8316 Rev 0 9/94
--	--	8318	N-Methylcarbamates by High Performance Liquid Chroma-tography (HPLC)	Vol IB Chap 4 Sec 4.3.3	8318 Rev 0 9/94

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	--	8321	Solvent Extractable Non-Volatile Compounds by High Performance Liquid Chromatography/Thermospray/Mass Spectrometry (HPLC/TSP/MS) or Ultraviolet (UV) Detection	Vol IB Chap 4 Sec 4.3.3	8321 Rev 0 9/94
--	--	8330	Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)	Vol IB Chap 4 Sec 4.3.3	8330 Rev 0 9/94
--	--	8331	Tetrazene by Reverse Phase High Performance Liquid Chromatography (HPLC)	Vol IB Chap 4 Sec 4.3.3	8331 Rev 0 9/94
--	--	8410	Gas Chromatography/Fourier Transform Infrared (GC/FT-IR) Spectrometry for Semivolatile Organics: Capillary Column	Vol IB Chap 4 Sec 4.3.4	8410 Rev 0 9/94
9010	9010A	--	Total and Amenable Cyanide (Colorimetric, Manual)	Vol IC Chap 5	9010A Rev 1 7/92
9012	--	--	Total and Amenable Cyanide (Colorimetric, Automated UV)	Vol IC Chap 5	9012 Rev 0 9/86

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	9013	--	Cyanide Extraction Procedure for Solids and Oils	Vol IC Chap 5	9013 Rev 0 7/92
9020	9020A	9020B	Total Organic Halides (TOX)	Vol IC Chap 5	9020B Rev 2 9/94
--	9021	--	Purgeable Organic Halides (POX)	Vol IC Chap 5	9021 Rev 0 7/92
9022	--	--	Total Organic Halides (TOX) by Neutron Activation Analysis	Vol IC Chap 5	9022 Rev 0 9/86
9030	9030A	--	Acid-Soluble and Acid-Insoluble Sulfides	Vol IC Chap 5	9030A Rev 1 7/92
--	9031	--	Extractable Sulfides	Vol IC Chap 5	9031 Rev 0 7/92
9035	--	--	Sulfate (Colorimetric, Automated, Chloranilate)	Vol IC Chap 5	9035 Rev 0 9/86
9036	--	--	Sulfate (Colorimetric, Automated, Methylthymol Blue, AA II)	Vol IC Chap 5	9036 Rev 0 9/86
9038	--	--	Sulfate (Turbidimetric)	Vol IC Chap 5	9038 Rev 0 9/86

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
9040	--	9040A	pH Electrometric Measurement	Vol IC Chap 6	9040A Rev 1 9/94
9041	9041A	--	pH Paper Method	Vol IC Chap 6	9041A Rev 1 7/92
9045	9045A	9045B	Soil and Waste pH	Vol IC Chap 6	9045B Rev 2 9/94
9050	--	--	Specific Conductance	Vol IC Chap 6	9050 Rev 0 9/86
--	--	9056	Determination of Inorganic Anions by Ion Chromatography	Vol IC Chap 5	9056 Rev 0 9/94
9060	--	--	Total Organic Carbon	Vol IC Chap 5	9060 Rev 0 9/86
9065	--	--	Phenolics (Spectrophotometric, Manual 4-AAP with Distillation)	Vol IC Chap 5	9065 Rev 0 9/86
9066	--	--	Phenolics (Colorimetric, Automated 4-AAP with Distillation)	Vol IC Chap 5	9066 Rev 0 9/86
9067	--	--	Phenolics (Spectrophotometric, MBTH with Distillation)	Vol IC Chap 5	9067 Rev 0 9/86

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
9070	--	--	Total Recoverable Oil & Grease (Gravimetric, Separatory Funnel Extraction)	Vol IC Chap 5	9070 Rev 0 9/86
9071	--	9071A	Oil and Grease Extraction Method for Sludge and Sediment Samples	Vol IC Chap 5	9071A Rev 1 9/94
--	--	9075	Test Method for Total Chlorine in New and Used Petroleum Products by X-Ray Fluorescence Spectrometry (XRF)	Vol IC Chap 5	9075 Rev 0 9/94
--	--	9076	Test Method for Total Chlorine in New and Used Petroleum Products by Oxidative Combustion and Microcoulometry	Vol IC Chap 5	9076 Rev 0 9/94
--	--	9077	Test Methods for Total Chlorine in New and Used Petroleum Products (Field Test Kit Methods)	Vol IC Chap 5	9077 Rev 0 9/94
9080	--	--	Cation-Exchange Capacity of Soils (Ammonium Acetate)	Vol IC Chap 6	9080 Rev 0 9/86
9081	--	--	Cation-Exchange Capacity of Soils (Sodium Acetate)	Vol IC Chap 6	9081 Rev 0 9/86

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
9090	9090A	--	Compatibility Test for Wastes and Membrane Liners	Vol IC Chap 6	9090A Rev 1 7/92
9095	--	--	Paint Filter Liquids Test	Vol IC Chap 6	9095 Rev 0 9/86
--	--	9096	Liquid Release Test (LRT) Procedure	Vol IC Chap 6	9096 Rev 0 9/94
9100	--	--	Saturated Hydraulic Conductivity, Saturated Leachate Conductivity, and Intrinsic Permeability	Vol IC Chap 6	9100 Rev 0 9/86
9131	--	--	Total Coliform: Multiple Tube Fermentation Technique	Vol IC Chap 5	9131 Rev 0 9/86
9132	--	--	Total Coliform: Membrane Filter Technique	Vol IC Chap 5	9132 Rev 0 9/86
9200	--	--	Nitrate	Vol IC Chap 5	9200 Rev 0 9/86
9250	--	--	Chloride (Colorimetric, Automated Ferricyanide AAI)	Vol IC Chap 5	9250 Rev 0 9/86
9251	--	--	Chloride (Colorimetric, Automated Ferricyanide AAII)	Vol IC Chap 5	9251 Rev 0 9/86

SW-846 METHOD STATUS TABLE (9/94), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FINAL UPDT. II DATED 9/94	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
9252	--	9252A	Chloride (Titrimetric, Mercuric Nitrate)	Vol IC Chap 5	9252A Rev 1 9/94
--	--	9253	Chloride (Titrimetric, Silver Nitrate)	Vol IC Chap 5	9253 Rev 0 9/94
9310	--	--	Gross Alpha and Gross Beta	Vol IC Chap 6	9310 Rev 0 9/86
9315	--	--	Alpha-Emitting Radium Isotopes	Vol IC Chap 6	9315 Rev 0 9/86
9320	--	--	Radium-228	Vol IC Chap 5	9320 Rev 0 9/86
HCN Test Method	HCN Test Method	HCN Test Method	Test Method to Determine Hydrogen Cyanide Released from Wastes	Vol IC Chap 7 Sec 7.3	Guidance Method Only
H_2S Test Method	H_2S Test Method	H_2S Test Method	Test Method to Determine Hydrogen Sulfide Released from Wastes	Vol IC Chap 7 Sec 7.3	Guidance Method Only

1020A

METHOD 1020A

SETAFLASH CLOSED-CUP METHOD FOR DETERMINING IGNITABILITY

1.0 SCOPE AND APPLICATION

1.1 Method 1020 makes use of the Setaflash Closed Tester to determine the flash point of liquids that have flash points between 0° and 110°C (32° and 230°F) and viscosities lower than 150 stokes at 25°C (77°F).

1.2 The procedure may be used to determine whether a material will or will not flash at a specified temperature or to determine the finite temperature at which a material will flash.

1.3 Liquids that tend to form surface films under test conditions or those that contain non-filterable suspended solids shall be tested for ignitability using Method 1010 (Pensky-Martens Closed-Cup).

2.0 SUMMARY OF METHOD

2.1 By means of a syringe, 2-mL of sample is introduced through a leak-proof entry port into the tightly closed Setaflash Tester or directly into the cup which has been brought to within 3°C (5°F) below the expected flash point.

2.2 As a flash/no-flash test, the expected flash-point temperature may be a specification (e.g., 60°C). For specification testing, the temperature of the apparatus is raised to the precise temperature of the specification flash point by slight adjustment of the temperature dial. After 1 minute, a test flame is applied inside the cup and note is taken as to whether the test sample flashes or not. If a repeat test is necessary, a fresh sample should be used.

2.3 For a finite flash management, the temperature is sequentially increased through the anticipated range, the test flame being applied at 5°C (9°F) intervals until a flash is observed. A repeat determination is then made using a fresh sample, starting the test at the temperature of the last interval before the flash point of the material and making tests at increasing 0.5°C (1°F) intervals.

For further information on how to conduct a test with this method, see Reference 1 below.

3.0 METHOD PERFORMANCE

See Method 1010.

4.0 REFERENCES

1. D-3278-78, Test Method for Flash Point of Liquids by Setaflash Closed Tester, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.

2. Umana, M., Gutknecht, W., Salmons, C., et al., Evaluation of Ignitability Methods (Liquids), EPA/600/S4-85/053, 1985.

3. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

METHOD 1110

CORROSIVITY TOWARD STEEL

1.0 SCOPE AND APPLICATION

1.1 Method 1110 is used to measure the corrosivity toward steel of both aqueous and nonaqueous liquid wastes.

2.0 SUMMARY OF METHOD

2.1 This test exposes coupons of SAE Type 1020 steel to the liquid waste to be evaluated and, by measuring the degree to which the coupon has been dissolved, determines the corrosivity of the waste.

3.0 INTERFERENCES

3.1 In laboratory tests, such as this one, corrosion of duplicate coupons is usually reproducible to within 10%. However, large differences in corrosion rates may occasionally occur under conditions where the metal surfaces become passivated. Therefore, at least duplicate determinations of corrosion rate should be made.

4.0 APPARATUS AND MATERIALS

4.1 An apparatus should be used, consisting of a kettle or flask of suitable size (usually 500 to 5,000 mL), a reflux condenser, a thermowell and temperature regulating device, a heating device (mantle, hot plate, or bath), and a specimen support system. A typical resin flask set up for this type of test is shown in Figure 1.

4.2 The supporting device and container shall be constructed of materials that are not affected by, or cause contamination of, the waste under test.

4.3 The method of supporting the coupons will vary with the apparatus used for conducting the test, but it should be designed to insulate the coupons from each other physically and electrically and to insulate the coupons from any metallic container or other device used in the test. Some common support materials include glass, fluorocarbon, or coated metal.

4.4 The shape and form of the coupon support should ensure free contact with the waste.

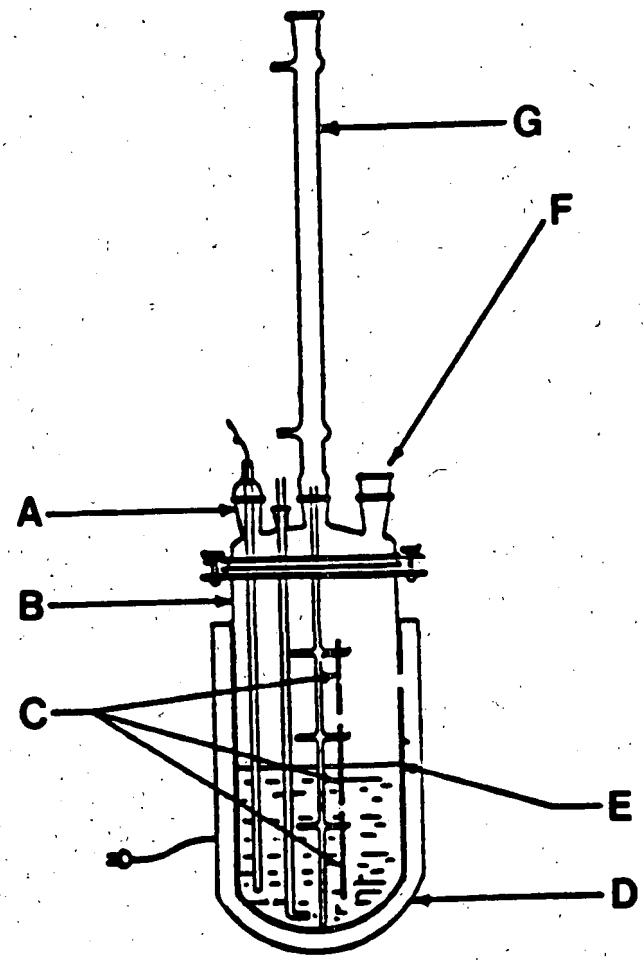


Figure 1. Typical resin flask that can be used as a versatile and convenient apparatus to conduct simple immersion tests. Configuration of the flask top is such that more sophisticated apparatus can be added as required by the specific test being conducted. A = thermowell, B = resin flask, C = specimens hung on supporting device, D = heating mantle, E = liquid interface, F = opening in flask for additional apparatus that may be required, and G = reflux condenser.

4.5 A circular specimen of SAE 1020 steel of about 3.75 cm (1.5 in.) diameter is a convenient shape for a coupon. With a thickness of approximately 0.32 cm (0.125 in.) and a 0.80-cm (0.4-in.)-diameter hole for mounting, these specimens will readily pass through a 45/50 ground-glass joint of a distillation kettle. The total surface area of a circular specimen is given by the following equation:

$$A = 3.14/2(D^2-d^2) + (t)(3.14)(D) + (t)(3.14)(d)$$

where:

t = thickness.
D = diameter of the specimen.
d = diameter of the mounting hole.

If the hole is completely covered by the mounting support, the last term in the equation, (t)(3.14)(d), is omitted.

4.5.1 All coupons should be measured carefully to permit accurate calculation of the exposed areas. An area calculation accurate to ±1% is usually adequate.

4.5.2 More uniform results may be expected if a substantial layer of metal is removed from the coupons prior to testing the corrosivity of the waste. This can be accomplished by chemical treatment (pickling), by electrolytic removal, or by grinding with a coarse abrasive. At least 0.254 mm (0.0001 in.) or 2-3 mg/cm^2 should be removed. Final surface treatment should include finishing with #120 abrasive paper or cloth. Final cleaning consists of scrubbing with bleach-free scouring powder, followed by rinsing in distilled water and then in acetone or methanol, and finally by air-drying. After final cleaning, the coupon should be stored in a desiccator until used.

4.5.3 The minimum ratio of volume of waste to area of the metal coupon to be used in this test is 40 mL/cm^2.

5.0 REAGENTS

5.1 Sodium hydroxide (NaOH), (20%): Dissolves 200 g NaOH in 800 mL Type II water and mix well.

5.2 Zinc dust.

5.3 Hydrochloric acid (HCl): Concentrated.

5.4 Stannous chloride ($SnCl_2$).

5.5 Antimony chloride ($SbCl_3$).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples should be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

7.0 PROCEDURE

7.1 Assemble the test apparatus as described in Paragraph 4.0, above.

7.2 Fill the container with the appropriate amount of waste.

7.3 Begin agitation at a rate sufficient to ensure that the liquid is kept well mixed and homogeneous.

7.4 Using the heating device, bring the temperature of the waste to 55°C (130°F).

7.5 An accurate rate of corrosion is not required; only a determination as to whether the rate of corrosion is less than or greater than 6.35 mm per year is required. A 24-hr test period should be ample to determine whether or not the rate of corrosion is >6.35 mm per year.

7.6 In order to determine accurately the amount of material lost to corrosion, the coupons have to be cleaned after immersion and prior to weighing. The cleaning procedure should remove all products of corrosion while removing a minimum of sound metal. Cleaning methods can be divided into three general categories: mechanical, chemical, and electrolytic.

7.6.1 Mechanical cleaning includes scrubbing, scraping, brushing, and ultrasonic procedures. Scrubbing with a bristle brush and mild abrasive is the most popular of these methods. The others are used in cases of heavy corrosion as a first step in removing heavily encrusted corrosion products prior to scrubbing. Care should be taken to avoid removing sound metal.

7.6.2 Chemical cleaning implies the removal of material from the surface of the coupon by dissolution in an appropriate solvent. Solvents such as acetone, dichloromethane, and alcohol are used to remove oil, grease, or resinous materials and are used prior to immersion to remove the products of corrosion. Solutions suitable for removing corrosion from the steel coupon are:

Solution	Soaking Time	Temperature
20% NaOH + 200 g/L zinc dust	5 min	Boiling
or		
Conc. HCl + 50 g/L $SnCl_2$ + 20 g/L $SbCl_3$	Until clean	Cold

7.6.3 Electrolytic cleaning should be preceded by scrubbing to remove loosely adhering corrosion products. One method of electrolytic cleaning that can be employed uses:

Solution:	50 g/L H_2SO_4
Anode:	Carbon or lead
Cathode:	Steel coupon
Cathode current density:	20 amp/cm^2 (129 amp/in.^{2})
Inhibitor:	2 cc organic inhibitor/liter
Temperature:	74°C (165°F)
Exposure Period:	3 min.

NOTE: Precautions must be taken to ensure good electrical contact with the coupon to avoid contamination of the cleaning solution with easily reducible metal ions and to ensure that inhibitor decomposition has not occurred. Instead of a proprietary inhibitor, 0.5 g/L of either diorthotolyl thiourea or quinolin ethiodide can be used.

7.7 Whatever treatment is employed to clean the coupons, its effect in removing sound metal should be determined by using a blank (i.e., a coupon that has not been exposed to the waste). The blank should be cleaned along with the test coupon and its waste loss subtracted from that calculated for the test coupons.

7.8 After corroded specimens have been cleaned and dried, they are reweighed. The weight loss is employed as the principal measure of corrosion. Use of weight loss as a measure of corrosion requires making the assumption that all weight loss has been due to generalized corrosion and not localized pitting. In order to determine the corrosion rate for the purpose of this regulation, the following formula is used:

$$\text{Corrosion Rate (mmpy)} = \frac{\text{weight loss} \times 11.145}{\text{area} \times \text{time}}$$

where: weight loss is in milligrams,
area in square centimeters,
time in hours, and
corrosion rate in millimeters per year (mmpy).

8.0 QUALITY CONTROL

8.1 All quality control data should be filed and available for auditing.

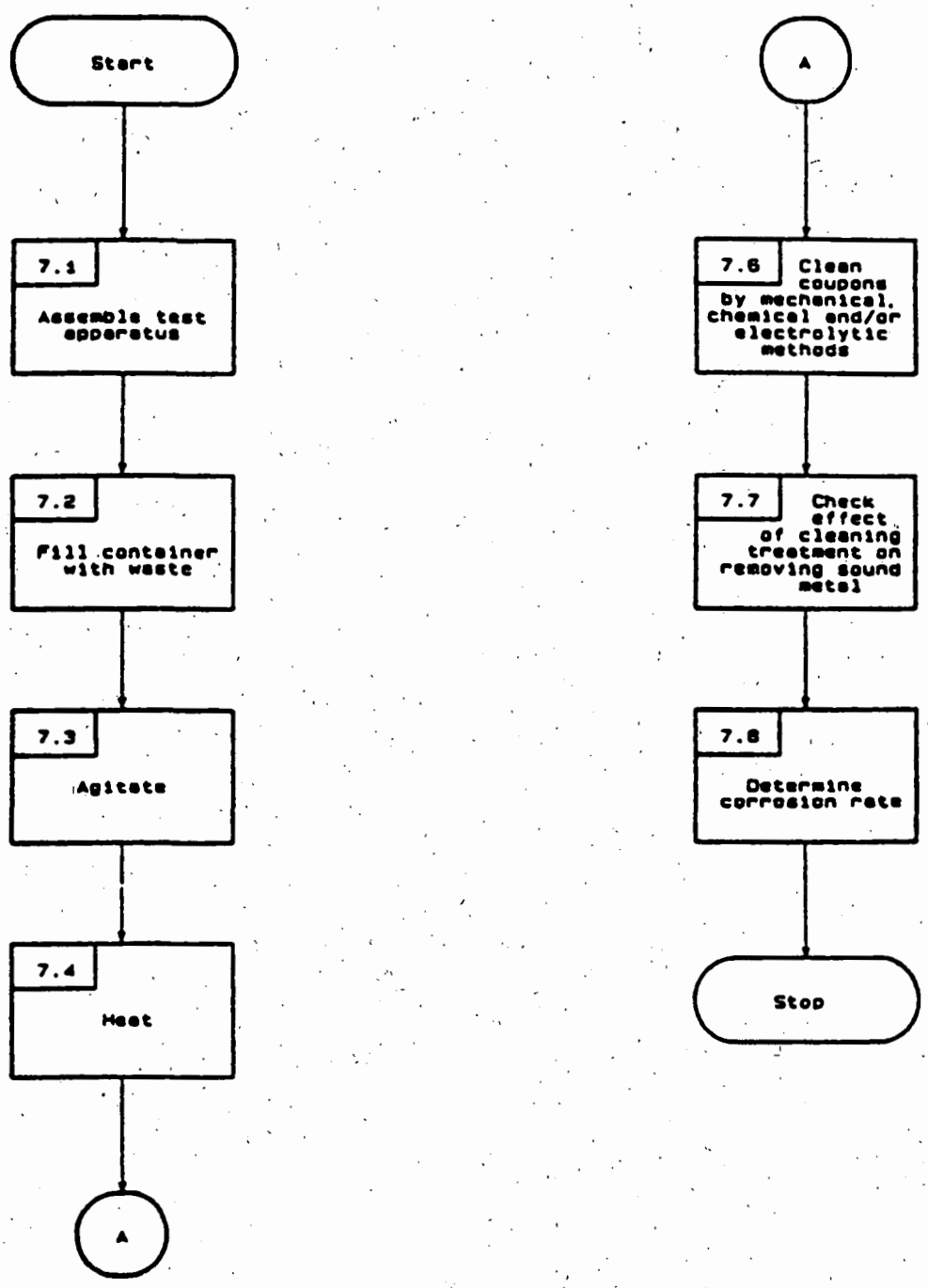
8.2 Duplicate samples should be analyzed on a routine basis.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. National Association of Corrosion Engineers, "Laboratory Corrosion Testing of Metals for the Process Industries," NACE Standard TM-01-69 (1972 Revision), NACE, 3400 West Loop South, Houston, TX 77027.



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1310A

METHOD 1310A

EXTRACTION PROCEDURE (EP) TOXICITY TEST METHOD AND STRUCTURAL INTEGRITY TEST

1.0 SCOPE AND APPLICATION

1.1 This method is an interim method to determine whether a waste exhibits the characteristic of Extraction Procedure Toxicity.

1.2 The procedure may also be used to simulate the leaching which a waste may undergo if disposed of in a sanitary landfill. Method 1310 is applicable to liquid, solid, and multiphase samples.

2.0 SUMMARY OF METHOD

2.1 If a representative sample of the waste contains > 0.5% solids, the solid phase of the sample is ground to pass a 9.5 mm sieve and extracted with deionized water which is maintained at a pH of 5 ± 0.2, with acetic acid. Wastes that contain < 0.5% filterable solids are, after filtering, considered to be the EP extract for this method. Monolithic wastes which can be formed into a cylinder 3.3 cm (dia) x 7.1 cm, or from which such a cylinder can be formed which is representative of the waste, may be evaluated using the Structural Integrity Procedure instead of being ground to pass a 9.5-mm sieve.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Extractor - For purposes of this test, an acceptable extractor is one that will impart sufficient agitation to the mixture to (1) prevent stratification of the sample and extraction fluid and (2) ensure that all sample surfaces are continuously brought into contact with well-mixed extraction fluid. Examples of suitable extractors are shown in Figures 1-3 of this method and are available from: Associated Designs & Manufacturing Co., Alexandria, Virginia; Glas-Col Apparatus Co., Terre Haute, Indiana; Millipore, Bedford, Massachusetts; and Rexnard, Milwaukee, Wisconsin.

4.2 pH meter or pH controller - Accurate to 0.05 pH units with temperature compensation.

4.3 Filter holder - Capable of supporting a 0.45-μm filter membrane and of withstanding the pressure needed to accomplish separation. Suitable filter holders range from simple vacuum units to relatively complex systems that can exert up to 5.3 kg/cm^3 (75 psi) of pressure. The type of filter holder used depends upon the properties of the mixture to be filtered. Filter holders known to EPA and deemed suitable for use are listed in Table 1.

4.4 Filter membrane - Filter membrane suitable for conducting the required filtration shall be fabricated from a material that (1) is not physically changed by the waste material to be filtered and (2) does not absorb or leach the chemical species for which a waste's EP extract will be analyzed. Table 2 lists filter media known to the agency to be suitable for solid waste testing.

4.4.1 In cases of doubt about physical effects on the filter, contact the filter manufacturer to determine if the membrane or the prefilter is adversely affected by the particular waste. If no information is available, submerge the filter in the waste's liquid phase. A filter that undergoes visible physical change after 48 hours (i.e., curls, dissolves, shrinks, or swells) is unsuitable for use.

4.4.2 To test for absorption or leaching by the filter:

4.4.2.1 Prepare a standard solution of the chemical species of interest.

4.4.2.2 Analyze the standard for its concentration of the chemical species.

4.4.2.3 Filter the standard and reanalyze. If the concentration of the filtrate differs from that of the original standard, then the filter membrane leaches or absorbs one or more of the chemical species and is not usable in this test method.

4.5 Structural integrity tester - A device meeting the specifications shown in Figure 4 and having a 3.18-cm (1.25-in) diameter hammer weighing 0.33 kg (0.73 lb) with a free fall of 15.24 cm (6 in) shall be used. This device is available from Associated Design and Manufacturing Company, Alexandria, VA 22314, as Part No. 125, or it may be fabricated to meet these specifications.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Acetic acid (0.5N), CH_3COOH. This can be made by diluting concentrated glacial acetic acid (17.5N) by adding 57 mL glacial acetic acid to 1,000 mL of water and diluting to 2 liters. The glacial acetic acid must be of high purity and monitored for impurities.

5.4 Analytical standards should be prepared according to the applicable analytical methods.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Preservatives must not be added to samples.

6.3 Samples can be refrigerated if it is determined that refrigeration will not affect the integrity of the sample.

7.0 PROCEDURE

7.1 If the waste does not contain any free liquid, go to Step 7.9. If the sample is liquid or multiphase, continue as follows. Weigh filter membrane and prefilter to ± 0.01 g. Handle membrane and prefilters with blunt curved-tip forceps or vacuum tweezers, or by applying suction with a pipet.

7.2 Assemble filter holder, membranes, and prefilters following the manufacturer's instructions. Place the 0.45-μm membrane on the support screen and add prefilters in ascending order of pore size. Do not prewet filter membrane.

7.3 Weigh out a representative subsample of the waste (100 g minimum).

7.4 Allow slurries to stand, to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration.

7.5 Wet the filter with a small portion of the liquid phase from the waste or from the extraction mixture. Transfer the remaining material to the filter holder and apply vacuum or gentle pressure (10-15 psi) until all liquid passes through the filter. Stop filtration when air or pressurizing gas moves through the membrane. If this point is not reached under vacuum or gentle pressure, slowly increase the pressure in 10-psi increments to 75 psi. Halt filtration when liquid flow stops. This liquid will constitute part or all of the extract (refer to Step 7.16). The liquid should be refrigerated until time of analysis.

NOTE: Oil samples or samples containing oil are treated in exactly the same way as any other sample. The liquid portion of the sample is filtered and treated as part of the EP extract. If the liquid portion of the sample will not pass through the filter (usually the case with heavy oils or greases), it should be carried through the EP extraction as a solid.

7.6 Remove the solid phase and filter media and, while not allowing them to dry, weigh to ± 0.01 g. The wet weight of the residue is determined by calculating the weight difference between the weight of the filters (Step 7.1) and the weight of the solid phase and the filter media.

7.7 The waste will be handled differently from this point on, depending on whether it contains more or less than 0.5% solids. If the sample appears to have < 0.5% solids, determine the percent solids exactly (see Note below) by the following procedure:

7.7.1 Dry the filter and residue at 80°C until two successive weighings yield the same value.

7.7.2 Calculate the percent solids, using the following equation:

$$\frac{\text{weight of filtered solid and filters} - \text{tared weight of filters}}{\text{initial weight of waste material}} \times 100 = \%\ \text{solids}$$

NOTE: This procedure is used only to determine whether the solid must be extracted or whether it can be discarded unextracted. It is not used in calculating the amount of water or acid to use in the extraction step. Do not extract solid material that has been dried at 80°C. A new sample will have to be used for extraction if a percent solids determination is performed.

7.8 If the solid constitutes < 0.5% of the waste, discard the solid and proceed immediately to Step 7.17, treating the liquid phase as the extract.

7.9 The solid material obtained from Step 7.5 and all materials that do not contain free liquids shall be evaluated for particle size. If the solid material has a surface area per g of material $\geq 3.1\ cm^2$ or passes through a 9.5-mm (0.375-in.) standard sieve, the operator shall proceed to Step 7.11. If the surface area is smaller or the particle size larger than specified above, the solid material shall be prepared for extraction by crushing, cutting, or grinding the material so that it passes through a 9.5-mm (0.375-in.) sieve or, if the material is in a single piece, by subjecting the material to the "Structural Integrity Procedure" described in Step 7.10.

7.10 Structural Integrity Procedure (SIP)

7.10.1 Cut a 3.3-cm diameter by 7.1-cm long cylinder from the waste material. If the waste has been treated using a fixation process, the waste may be cast in the form of a cylinder and allowed to cure for 30 days prior to testing.

7.10.2 Place waste into sample holder and assemble the tester. Raise the hammer to its maximum height and drop. Repeat 14 additional times.

7.10.3 Remove solid material from tester and scrape off any particles adhering to sample holder. Weigh the waste to the nearest 0.01 g and transfer it to the extractor.

7.11 If the sample contains > 0.5% solids, use the wet weight of the solid phase (obtained in Step 7.6) to calculate the amount of liquid and acid to employ for extraction by using the following equation:

$$W = W_f - W_t$$

where :

W = Wet weight in g of solid to be charged to extractor.

W_f = Wet weight in g of filtered solids and filter media.

W_t = Weight in g of tared filters.

If the waste does not contain any free liquids, 100 g of the material will be subjected to the extraction procedure.

7.12 Place the appropriate amount of material (refer to Step 7.11) into the extractor and add 16 times its weight with water.

7.13 After the solid material and water are placed in the extractor, the operator shall begin agitation and measure the pH of the solution in the extractor. If the pH is > 5.0, the pH of the solution should be decreased to 5.0 ± 0.2 by slowly adding 0.5N acetic acid. If the pH is ≤ 5.0, no acetic acid should be added. The pH of the solution should be monitored, as described below, during the course of the extraction, and, if the pH rises above 5.2, 0.5N acetic acid should be added to bring the pH down to 5.0 ± 0.2. However, in no event shall the aggregate amount of acid added to the solution exceed 4 mL of acid per g of solid. The mixture should be agitated for 24 hours and maintained at 20-40°C (68-104°F) during this time. It is recommended that the operator monitor and adjust the pH during the course of the extraction with a device such as the Type 45-A pH Controller, manufactured by Chemtrix, Inc., Hillsboro, Oregon 97123, or its equivalent, in conjunction with a metering pump and reservoir of 0.5N acetic acid. If such a system is not available, the following manual procedure shall be employed.

NOTE: Do not add acetic acid too quickly. Lowering the pH to below the target concentration of 5.0 could affect the metal concentrations in the leachate.

7.13.1 A pH meter should be calibrated in accordance with the manufacturer's specifications.

7.13.2 The pH of the solution should be checked, and, if necessary, 0.5 N acetic acid should be manually added to the extractor until the pH reaches 5.0 ± 0.2. The pH of the solution should be adjusted at 15-, 30-, and 60-minute intervals, moving to the next longer interval if the pH does not have to be adjusted > 0.5 pH units.

7.13.3 The adjustment procedure should be continued for at least 6 hours.

7.13.4 If, at the end of the 24-hour extraction period, the pH of the solution is not below 5.2 and the maximum amount of acid (4 mL per g of solids) has not been added, the pH should be adjusted to 5.0 ± 0.2 and the extraction continued for an additional 4 hours, during which the pH should be adjusted at 1-hour intervals.

7.14 At the end of the extraction period, water should be added to the extractor in an amount determined by the following equation:

$$V = (20)(W) - 16(W) - A$$

where:

V = mL water to be added.

W = Weight in g of solid charged to extractor.

A = mL of 0.5N acetic acid added during extraction.

7.15 The material in the extractor should be separated into its component liquid and solid phases in the following manner:

7.15.1 Allow slurries to stand to permit the solid phase to settle (wastes that are slow to settle may be centrifuged prior to filtration) and set up the filter apparatus (refer to Steps 4.3 and 4.4).

7.15.2 Wet the filter with a small portion of the liquid phase from the waste or from the extraction mixture. Transfer the remaining material to the filter holder and apply vacuum or gentle pressure (10-15 psi) until all liquid passes through the filter. Stop filtration when air or pressurizing gas moves through the membrane. If this point is not reached under vacuum or gentle pressure, slowly increase the pressure in 10-psi increments to 75 psi. Halt filtration when liquid flow stops.

7.16 The liquids resulting from Steps 7.5 and 7.15 should be combined. This combined liquid (or waste itself, if it has < 0.5% solids, as noted in Step 7.8) is the extract.

7.17 The extract is then prepared and analyzed using the appropriate analytical methods described in Chapters Three and Four of this manual.

NOTE: If the EP extract includes two phases, concentration of contaminants is determined by using a simple weighted average. For example: An EP extract contains 50 mL of oil and 1,000 mL of an aqueous phase. Contaminant concentrations are determined for each phase. The final contamination concentration is taken to be:

$$\frac{\left(50 \times \text{contaminant conc. in oil}\right) + \left(1{,}000 \times \text{contaminant conc. of aqueous phase}\right)}{1050}$$

NOTE: In cases where a contaminant was not detected, use the MDL in the calculation. For example, if the MDL in the oily phase is 100 mg/L and 1 mg/L in the aqueous phase, the reporting limit would be 6 mg/L (rounded to the nearest mg). If the regulatory threshold is 5 mg/L, the waste may be EP toxic and results of the analysis are inconclusive.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 All quality control measures described in Cnapter One and in the referenced analytical methods should be followed.

9.0 METHOD PERFORMANCE

9.1 The data tabulated in Table 3 were obtained from records of state and contractor laboratories and are intended to show the precision of the entire method (1310 plus analysis method).

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

3. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. EPA-APPROVED FILTER HOLDERS

Manufacturer	Size	Model No.	Comments
Vacuum Filters			
Gelman	47 mm	4011	
Nalgene	500 mL	44-0045	Disposable plastic unit, including prefilter, filter pads, and reservoir; can be used when solution is to be analyzed for inorganic constituents.
Nuclepore	47 mm	410400	
Millipore	47 mm	XX10 047 00	
Pressure Filters			
Nuclepore	142 mm	425900	
Micro Filtration Systems	142 mm	302300	
Millipore	142 mm	YT30 142 HW	

TABLE 2. EPA-APPROVED FILTRATION MEDIA

Supplier	Filter to be used for aqueous systems	Filter to be used for organic systems
Coarse prefilter		
Gelman	61631, 61635	61631, 61635
Nuclepore	210907, 211707	210907, 211707
Millipore	AP25 035 00, AP25 127 50	AP25 035 00, AP25 127 50
Medium prefilters		
Gelman	61654, 61655	
Nuclepore	210905, 211705	210905, 211705
Millipore	AP20 035 00, AP20 124 50	AP20 035 00, AP20 124 50
Fine prefilters		
Gelman	64798, 64803	64798, 64803
Nuclepore	210903, 211703	210903, 211703
Millipore	AP15 035 00, AP15 124 50	AP15 035 00, AP15 124 50
Fine filters (0.45 μm)		
Gelman	63069, 66536	60540 or 66149, 66151
Pall	NX04750, NX14225	
Nuclepore	142218	142218[a]
Millipore	HAWP 047 00, HAWP 142 50	FHUP 047 00, FHLP 142 50
Selas	83485-02, 83486-02	83485-02, 83486-02

[a]Susceptible to decomposition by certain polar organic solvents.

TABLE 3. PRECISIONS OF EXTRACTION-ANALYSIS PROCEDURES FOR SEVERAL ELEMENTS

Element	Sample Matrix	Analysis Method	Laboratory Replicates
Arsenic	1. Auto fluff	7060	1.8, 1.5 µg/L
	2. Barrel sludge	7060	0.9, 2.6 µg/L
	3. Lumber treatment company sediment	7060	28, 42 mg/L
Barium	1. Lead smelting emission control dust	6010	0.12, 0.12 mg/L
	2. Auto fluff	7081	791, 780 µg/L
	3. Barrel sludge	7081	422, 380 µg/L
Cadmium	1. Lead smelting emission control dust	3010/7130	120, 120 mg/L
	2. Wastewater treatment sludge from electroplating	3010/7130	360, 290 mg/L
	3. Auto fluff	7131	470, 610 µg/L
	4. Barrel sludge	7131	1100, 890 µg/L
	5. Oil refinery tertiary pond sludge	7131	3.2, 1.9 µg/L
Chromium	1. Wastewater treatment sludge from electroplating	3010/7190	1.1, 1.2 mg/L
	2. Paint primer	7191	61, 43 µg/L
	3. Paint primer filter	7191	--
	4. Lumber treatment company sediment	7191	0.81, 0.89 mg/L
	5. Oil refinery tertiary pond sludge	7191	--
Mercury	1. Barrel sludge	7470	0.15, 0.09 µg/L
	2. Wastewater treatment sludge from electroplating	7470	1.4, 0.4 µg/L
	3. Lead smelting emission control dust	7470	0.4, 0.4 µg/L

TABLE 3 (Continued)

Element	Sample Matrix	Analysis Method	Laboratory Replicates
Lead	1. Lead smelting emission control dust	3010/7420	940, 920 mg/L
	2. Auto fluff	7421	1540, 1490 µg/L
	3. Incinerator ash	7421	1000, 974 µg/L
	4. Barrel sludge	7421	2550, 2800 µg/L
	5. Oil refinery tertiary pond sludge	7421	31, 29 µg/L
Nickel	1. Sludge	7521	2260, 1720 µg/L
	2. Wastewater treatment sludge from electroplating	3010/7520	130, 140 mg/L
Chromium(VI)	1. Wastewater treatment sludge from electroplating	7196	18, 19 µg/L

FIGURE 1.
EXTRACTOR

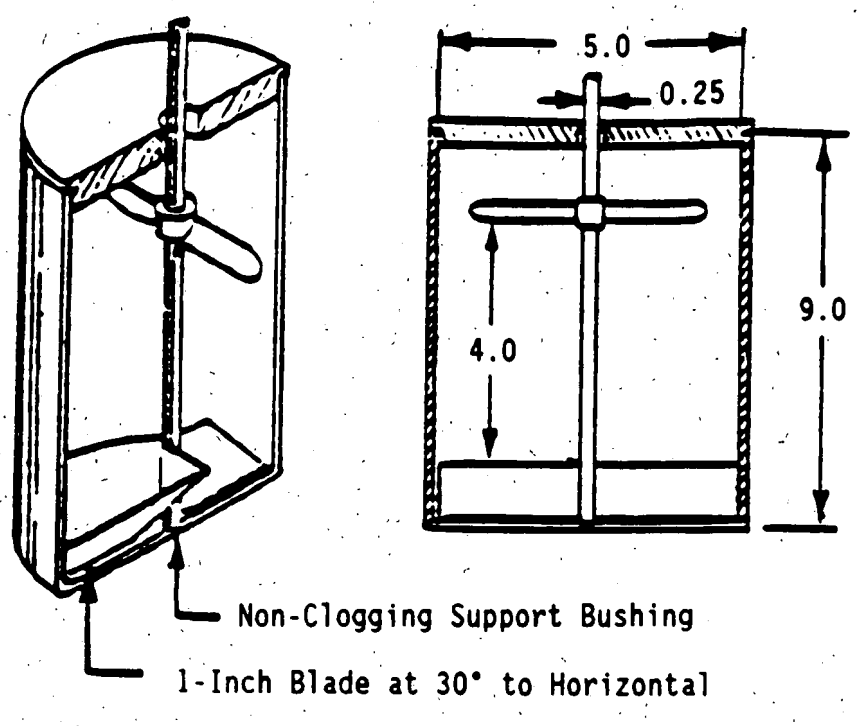


FIGURE 2.
ROTARY EXTRACTOR

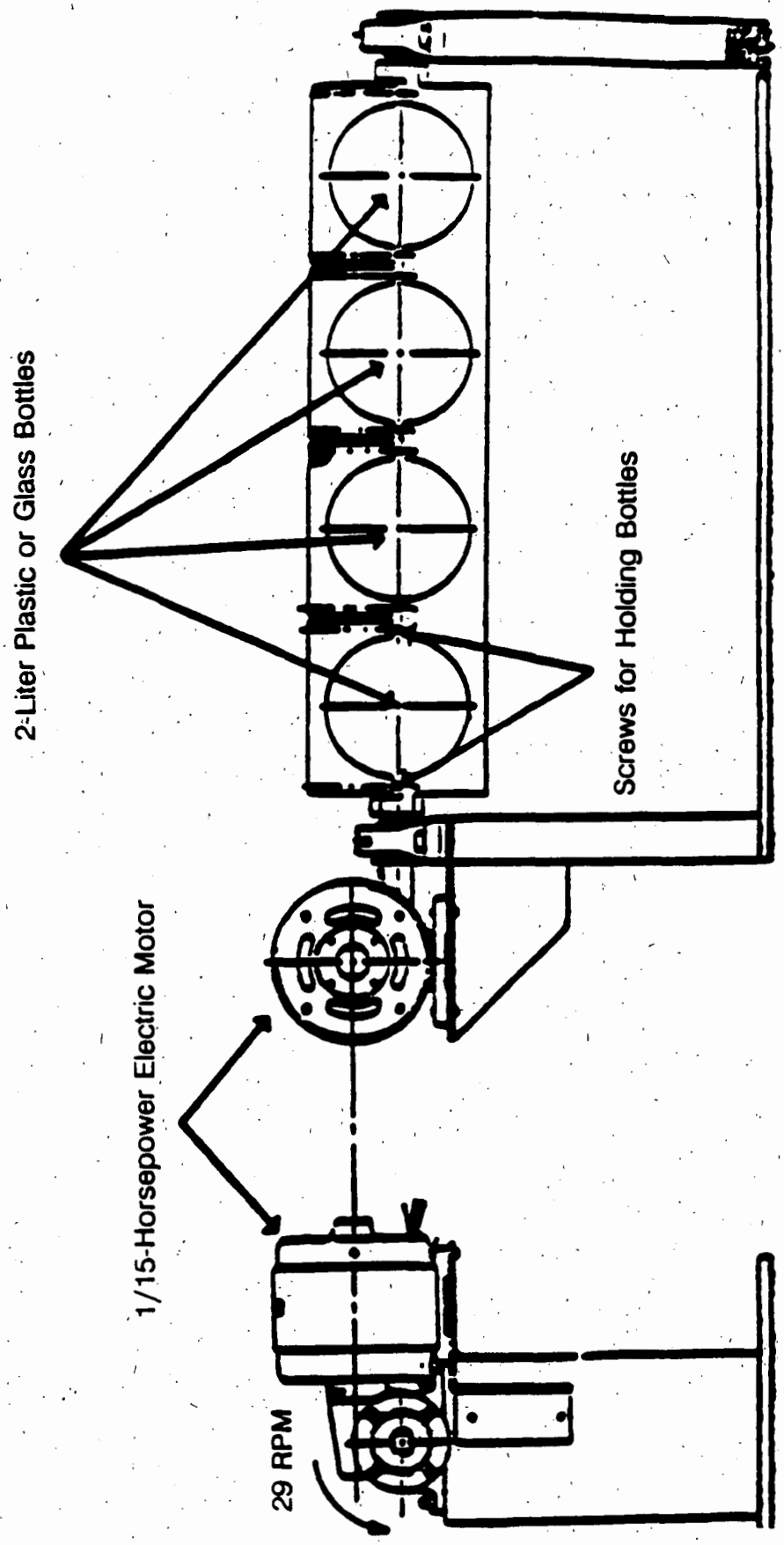


FIGURE 3.
EPRI EXTRACTOR

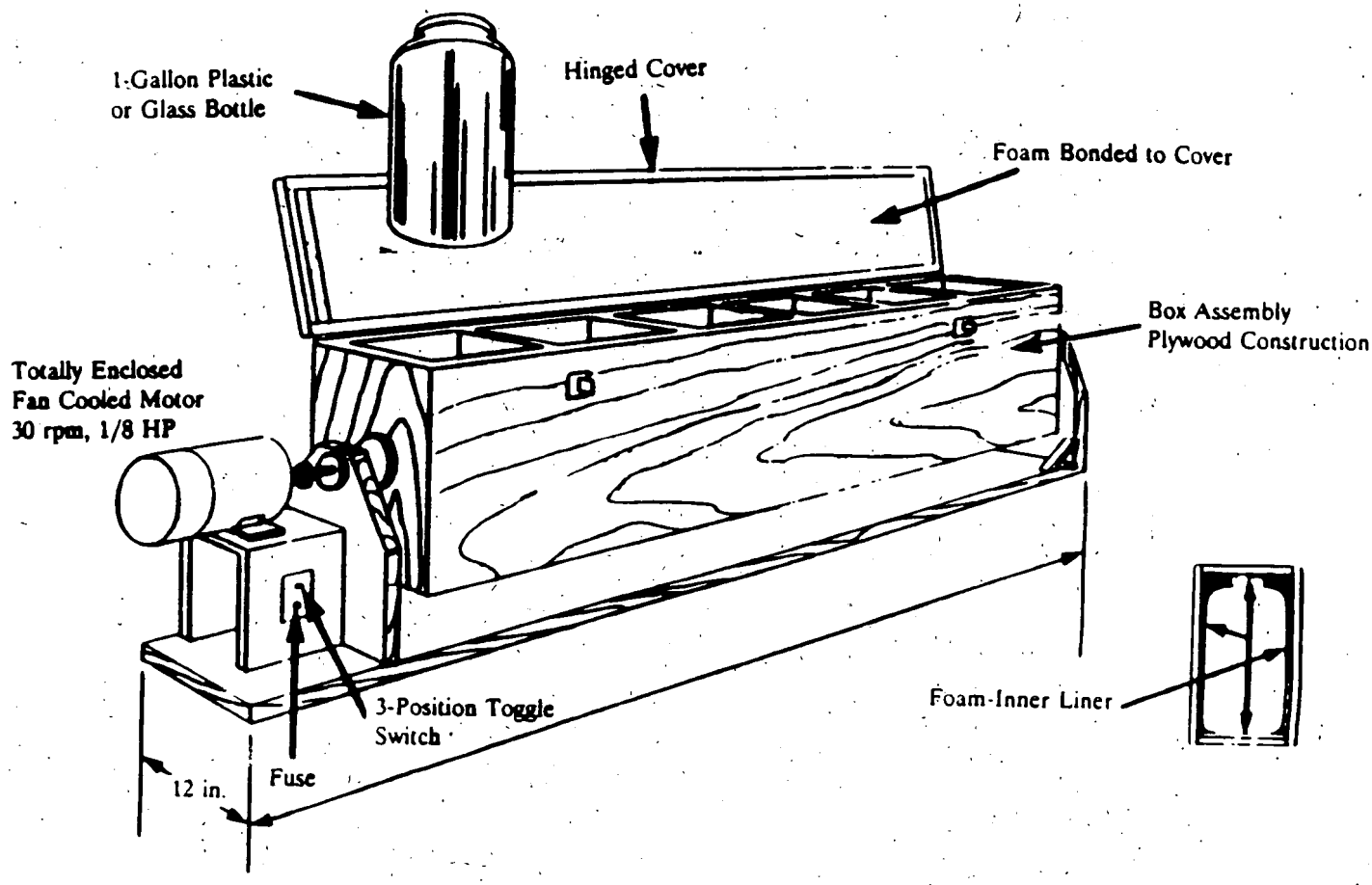
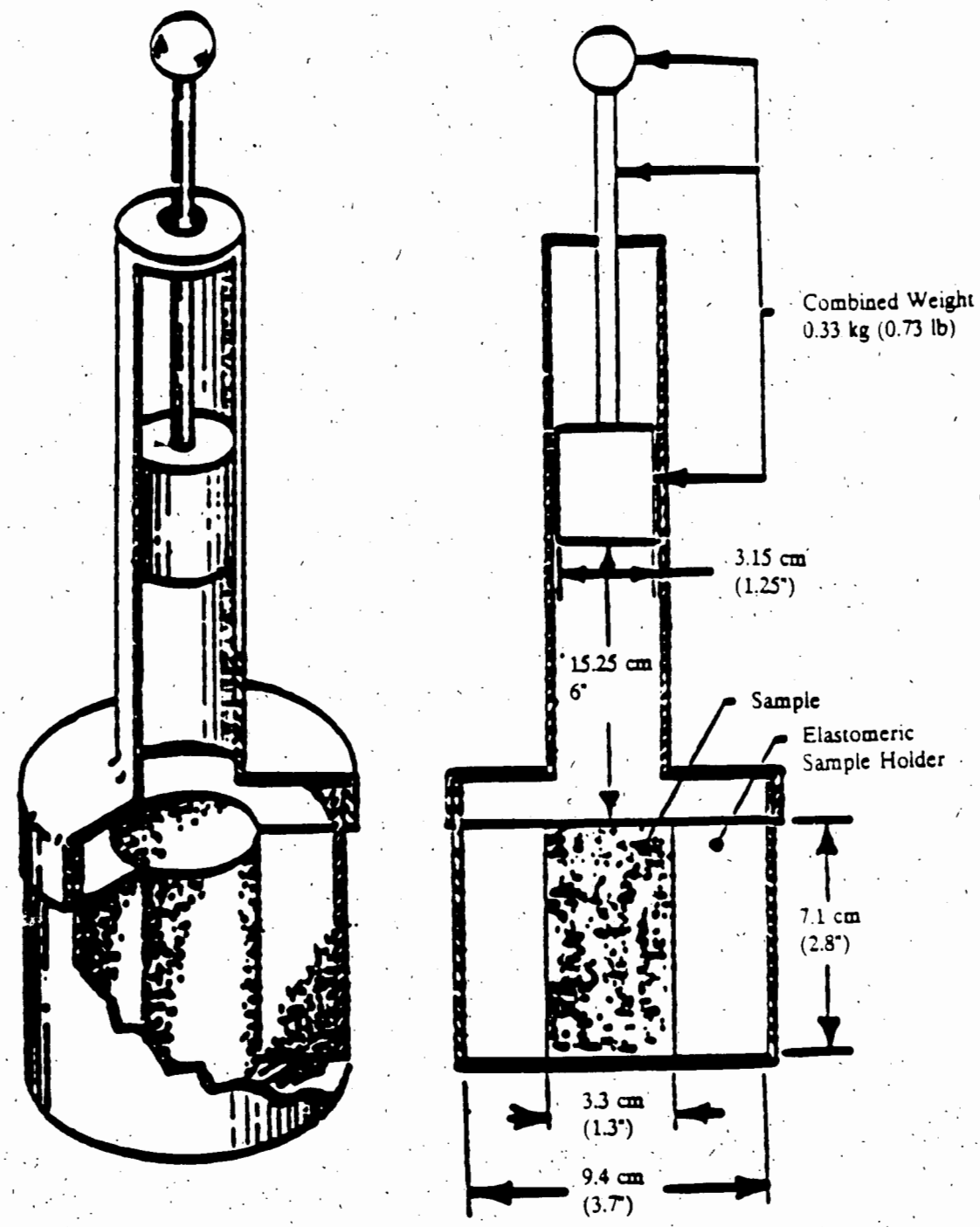
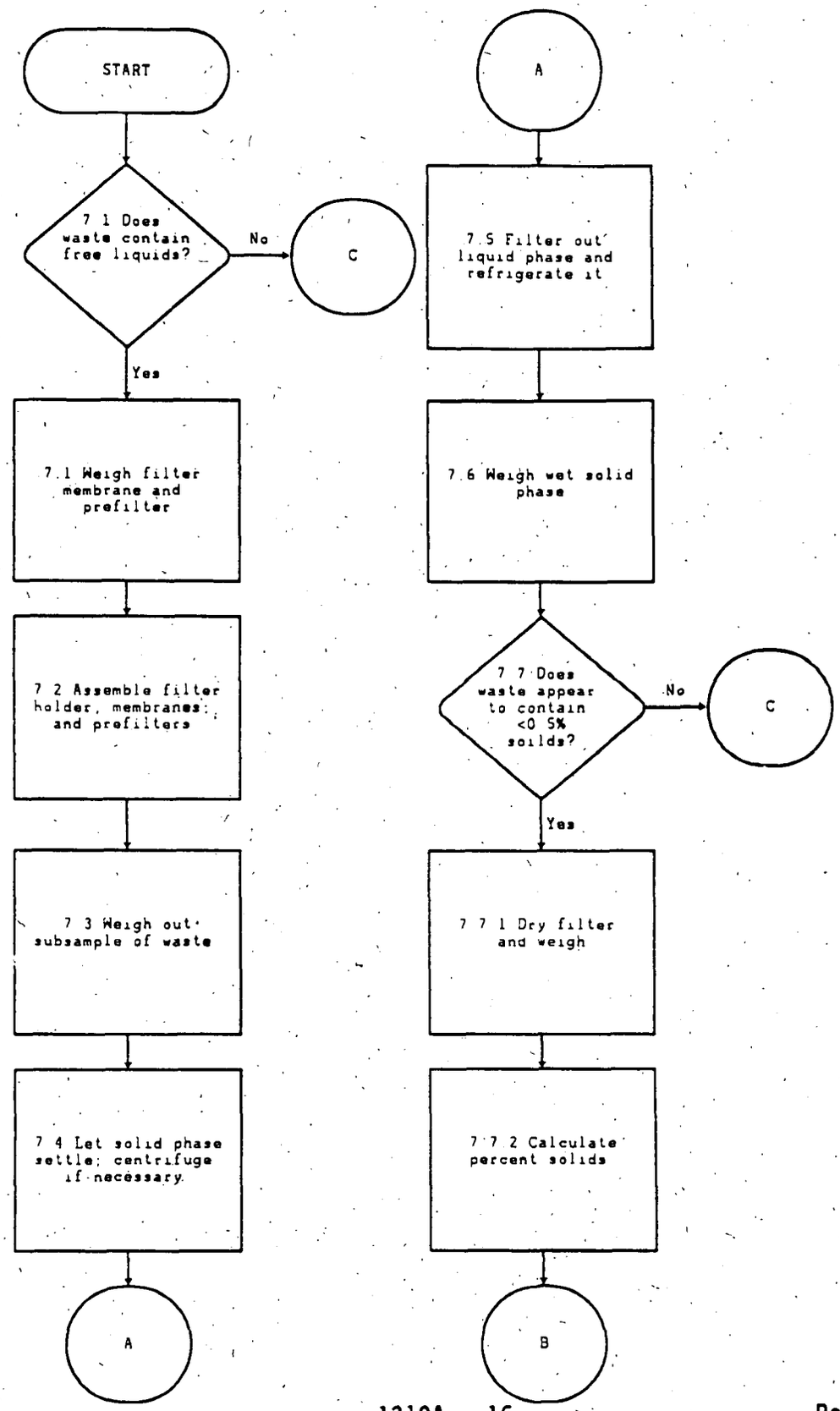
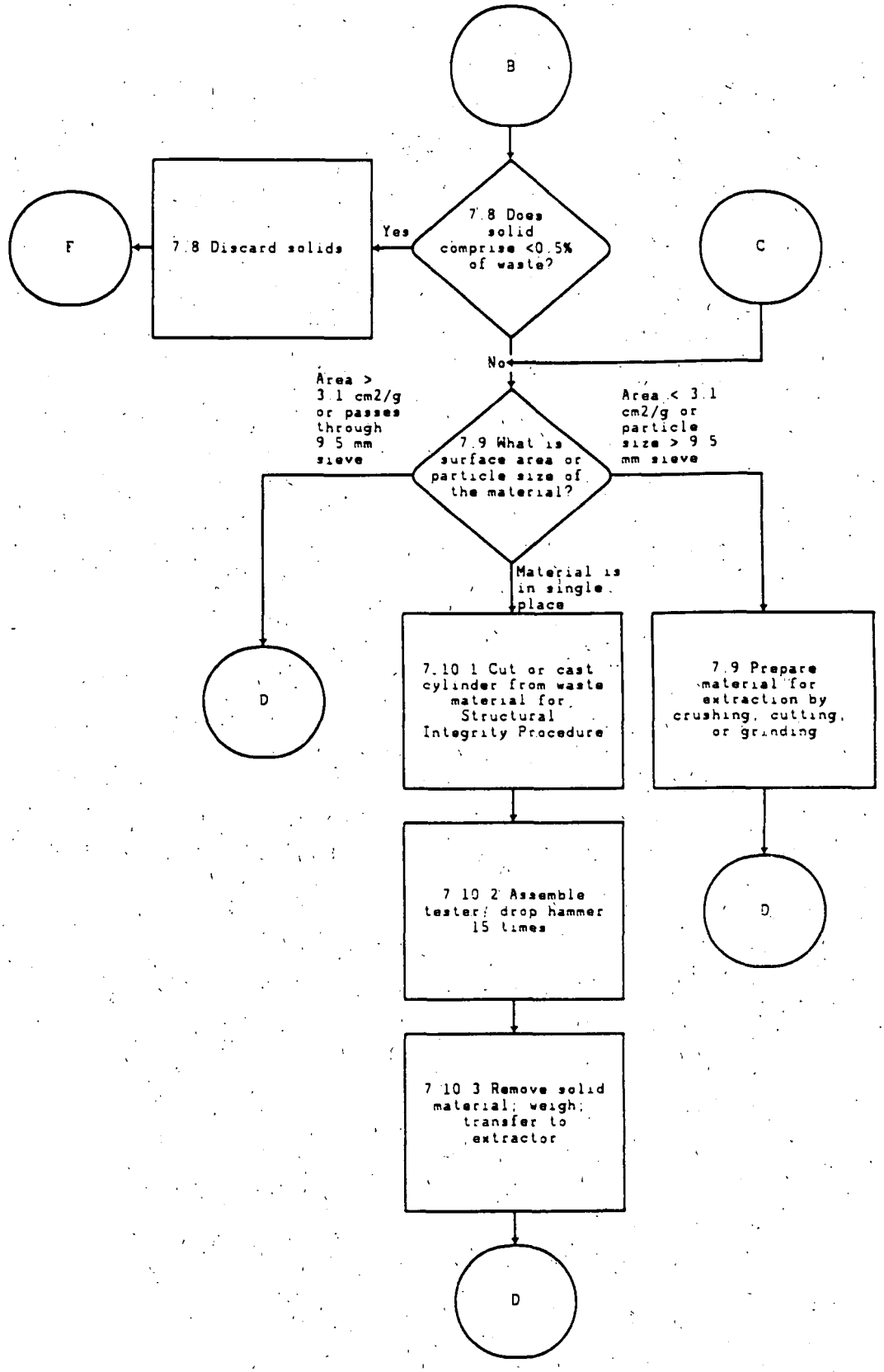
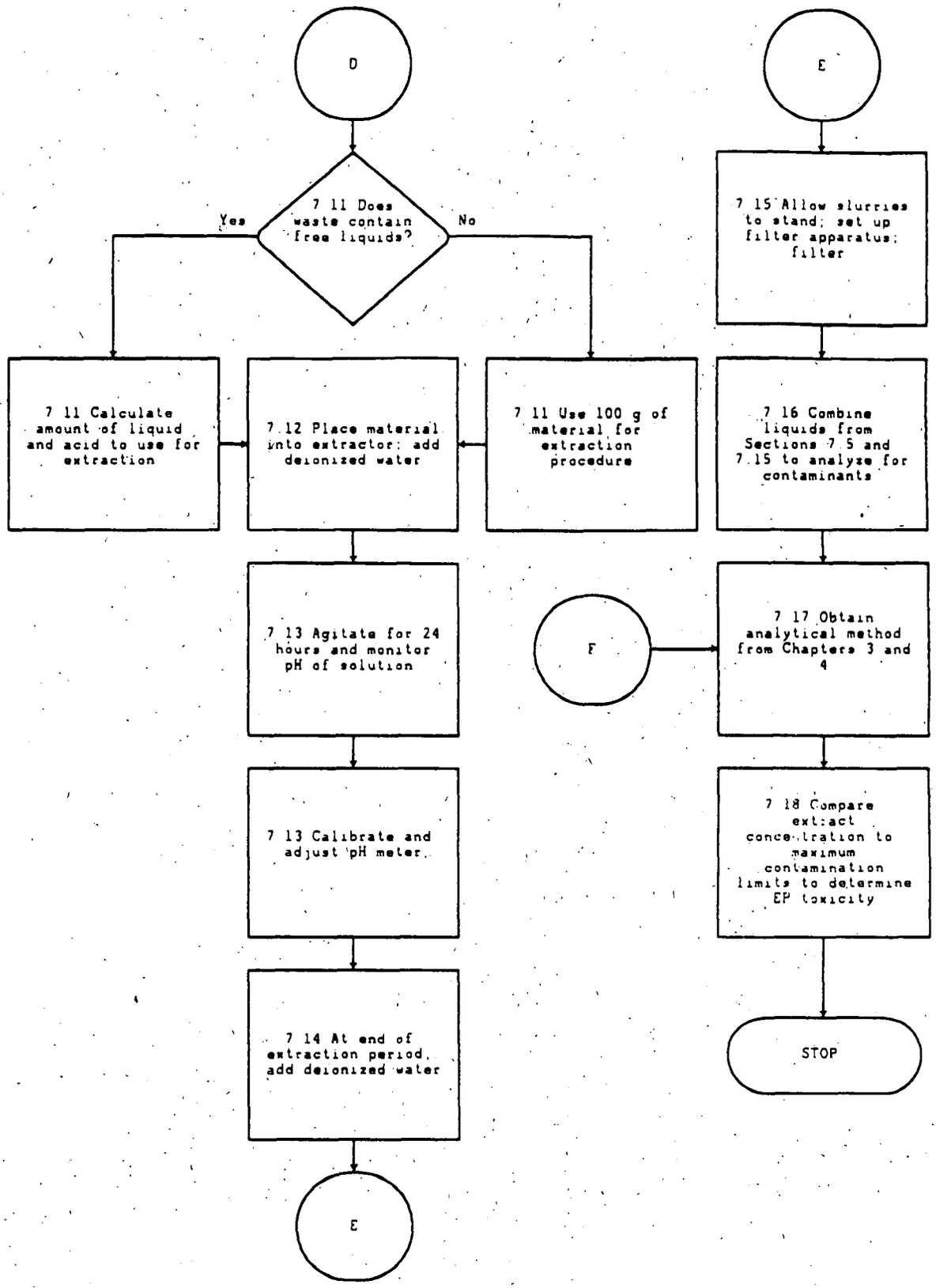


FIGURE 4.
COMPACTION TESTER




START
7 1 Does waste contain free liquids?
No
C
Yes
7.1 Weigh filter membrane and prefilter
7 2 Assemble filter holder, membranes, and prefilters
7 3 Weigh out subsample of waste
7 4 Let solid phase settle; centrifuge if necessary
A
A
7.5 Filter out liquid phase and refrigerate it
7.6 Weigh wet solid phase
7 7 Does waste appear to contain <0 5% soilds?
No
C
Yes
7 7 1 Dry filter and weigh
7 7 2 Calculate percent solids
B


B
7.8 Does solid comprise <0.5% of waste?
Yes
7.8 Discard solids
F
C
No
7.9 What is surface area or particle size of the material?
Area > 3.1 cm2/g or passes through 9.5 mm sieve
Area < 3.1 cm2/g or particle size > 9.5 mm sieve
Material is in single place
D
7.10.1 Cut or cast cylinder from waste material for Structural Integrity Procedure
7.9 Prepare material for extraction by crushing, cutting, or grinding
7.10.2 Assemble tester; drop hammer 15 times
D
7.10.3 Remove solid material; weigh; transfer to extractor
D


D
7 11 Does waste contain free liquids?
Yes
No
7 11 Calculate amount of liquid and acid to use for extraction
7 12 Place material into extractor; add deionized water
7 11 Use 100 g of material for extraction procedure
7 13 Agitate for 24 hours and monitor pH of solution
7 13 Calibrate and adjust pH meter
7 14 At end of extraction period, add deionized water
E
E
7 15 Allow slurries to stand; set up filter apparatus; filter
7 16 Combine liquids from Sections 7 5 and 7 15 to analyze for contaminants
F
7 17 Obtain analytical method from Chapters 3 and 4
7 18 Compare extract concentration to maximum contamination limits to determine EP toxicity
STOP

METHOD 1311

TOXICITY CHARACTERISTIC LEACHING PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.

1.2 If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run.

1.3 If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high concentrations that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

1.4 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the ZHE is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level.

2.0 SUMMARY OF METHOD

2.1 For liquid wastes (i.e., those containing less than 0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8 µm glass fiber filter, is defined as the TCLP extract.

2.2 For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile analytes (see Table 1 for a list of volatile compounds). Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 µm glass fiber filter.

2.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 1) at 30 ± 2 rpm. Suitable devices known to EPA are identified in Table 2.

4.2 Extraction Vessels

4.2.1 Zero-Headspace Extraction Vessel (ZHE). This device is for use only when the waste is being tested for the mobility of volatile analytes (i.e., those listed in Table 1). The ZHE (depicted in Figure 2) allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel (see Section 4.3.1). The vessels shall have an internal volume of 500-600 mL, and be equipped to accommodate a 90-110 mm filter. The devices contain VITON®[1] O-rings which should be replaced frequently. Suitable ZHE devices known to EPA are identified in Table 3.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for TCLP analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedure (see Section 7.3) refers to pounds per square inch (psi), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

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[1] VITON® is a trademark of Du Pont.

4.2.2 Bottle Extraction Vessel. When the waste is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste (see Section 4.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Section 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.3 Filtration Devices: It is recommended that all filtrations be performed in a hood.

4.3.1 Zero-Headspace Extractor Vessel (ZHE): When the waste is evaluated for volatiles, the zero-headspace extraction vessel described in Section 4.2.1 is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psi).

NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.3.2 Filter Holder: When the waste is evaluated for other than volatile analytes, any filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered (see Section 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (<10%) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration. Suitable filter holders known to EPA are shown in Table 4.

4.3.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb waste components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) may be used only when evaluating the mobility of metals. Borosilicate glass bottles are recommended for use over other types of glass bottles, especially when inorganics are analytes of concern.

4.4 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8 μm, or equivalent. Filters known to EPA which meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1 L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters: The meter should be accurate to ± 0.05 units at 25 °C.

4.6 ZHE Extract Collection Devices: TEDLAR®[2] bags or glass, stainless steel or PTFE gas-tight syringes are used to collect the initial liquid phase and the final extract of the waste when using the ZHE device. The devices listed are recommended for use under the following conditions:

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., <1% of total waste), the TEDLAR® bag or a 600 mL syringe should be used to collect and combine the initial liquid and solid extract.

4.6.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., >1% of total waste), the syringe or the TEDLAR® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100% solid) or has no significant solid phase (is 100% liquid), either the TEDLAR® bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g., a positive displacement or peristaltic pump, a gas tight syringe, pressure filtration unit (see Section 4.3.2), or other ZHE device).

4.8 Laboratory Balance: Any laboratory balance accurate to within ± 0.01 grams may be used (all weight measurements are to be within ± 0.1 grams).

4.9 Beaker or Erlenmeyer flask, glass, 500 mL.

4.10 Watchglass, appropriate diameter to cover beaker or Erlenmeyer flask.

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[2] TEDLAR® is a registered trademark of Du Pont.

4.11 Magnetic stirrer.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water is defined as water in which an interferant is not observed at or above the method's detection limit of the analyte(s) of interest. For nonvolatile extractions, ASTM Type II water or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.2.1 Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing about 500 grams of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.2.2 A water purification system (Millipore Super-Q or equivalent) may also be used to generate reagent water for volatile extractions.

5.2.3 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at 90 $\pm$ 5 degrees C, bubble a contaminant-free inert gas (e.g. nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow mouth screw-cap bottle under zero-headspace and seal with a Teflon-lined septum and cap.

5.3 Hydrochloric acid (1N), HCl, made from ACS reagent grade.

5.4 Nitric acid (1N), HNO_3, made from ACS reagent grade.

5.5 Sodium hydroxide (1N), NaOH, made from ACS reagent grade.

5.6 Glacial acetic acid, CH_3CH_2OOH, ACS reagent grade.

5.7 Extraction fluid.

5.7.1 Extraction fluid # 1: Add 5.7 mL glacial CH_3CH_2OOH to 500 mL of reagent water (See Section 5.2), add 64.3 mL of 1N NaOH, and dilute to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 4.93 $\pm$ 0.05.

5.7.2 Extraction fluid # 2: Dilute 5.7 mL glacial CH_3CH_2OOH with reagent water (See Section 5.2) to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88 $\pm$ 0.05.

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

5.8 Analytical standards shall be prepared according to the appropriate analytical method.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples shall be collected using an appropriate sampling plan.

6.2 The TCLP may place requirements on the minimal size of the field sample, depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for preliminary evaluation of which extraction fluid is to be used for the nonvolatile analyte extraction procedure. Another aliquot may be needed to actually conduct the nonvolatile extraction (see Section 1.4 concerning the use of this extract for volatile organics). If volatile organics are of concern, another aliquot may be needed. Quality control measures may require additional aliquots. Further, it is always wise to collect more sample just in case something goes wrong with the initial attempt to conduct the test.

6.3 Preservatives shall not be added to samples before extraction.

6.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.5 When the waste is to be evaluated for volatile analytes, care shall be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon-lined septum capped vials and stored at 4 °C. Samples should be opened only immediately prior to extraction).

6.6 TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs (see Section 7.2.14 if precipitation occurs). Extracts should be preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for organic analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See Section 8.0 (QA requirements) for acceptable sample and extract holding times.

7.0 PROCEDURE

7.1 Preliminary Evaluations

Perform preliminary TCLP evaluations on a minimum 100 gram aliquot of waste. This aliquot may not actually undergo TCLP extraction. These preliminary evaluations include: (1) determination of the percent solids (Section 7.1.1); (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (Section 7.1.2); (3) determination of whether the solid portion of the waste requires particle size reduction (Section 7.1.3); and (4) determination of which of the two extraction fluids are to be used for the nonvolatile TCLP extraction of the waste (Section 7.1.4).

7.1.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solids) proceed to Section 7.1.3.

7.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.1.1.3 through 7.1.1.9.

7.1.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.1.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.1.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight.

7.1.1.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.1.1.7 Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and

subtract it from the sample weight determined in Section 7.1.1.5 to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2 minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.1.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Section 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.1.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Section 7.1.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the waste sample by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in Section 7.1.1.5 or 7.1.1.7.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (Section 7.1.1.9)}}{\text{Total weight of waste (Section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2 If the percent solids determined in Section 7.1.1.9 is equal to or greater than 0.5%, then proceed either to Section 7.1.3 to determine whether the solid material requires particle size reduction or to Section 7.1.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined in Section 7.1.1.9 is less than 0.5%, then proceed to Section 7.2.9 if the

nonvolatile TCLP is to be performed and to Section 7.3 with a fresh portion of the waste if the volatile TCLP is to be performed.

7.1.2.1 Remove the solid phase and filter from the filtration apparatus.

7.1.2.2 Dry the filter and solid phase at 100 ± 20 °C until two successive weighing yield the same value within ± 1%. Record the final weight.

NOTE: Caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

7.1.2.3 Calculate the percent dry solids as follows:

$$\text{Percent dry solids} = \frac{\text{(Wt. of dry waste + filter) - tared wt. of filter}}{\text{Initial wt. of waste (Section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2.4 If the percent dry solids is less than 0.5%, then proceed to Section 7.2.9 if the nonvolatile TCLP is to be performed, and to Section 7.3 if the volatile TCLP is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile TCLP is to be performed, return to the beginning of this Section (7.1) and, with a fresh portion of waste, determine whether particle size reduction is necessary (Section 7.1.3) and determine the appropriate extraction fluid (Section 7.1.4). If only the volatile TCLP is to be performed, see the note in Section 7.1.4.

7.1.3 Determination of whether the waste requires particle size reduction (particle size is reduced during this step): Using the solid portion of the waste, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see Section 7.3.6).

NOTE: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

7.1.4 Determination of appropriate extraction fluid: If the solid content of the waste is greater than or equal to 0.5% and if the sample will be extracted for nonvolatile constituents (Section 7.2), determine the appropriate fluid (Section 5.7) for the nonvolatiles extraction as follows:

NOTE: TCLP extraction for volatile constituents uses only extraction fluid #1 (Section 5.7.1). Therefore, if TCLP extraction for nonvolatiles is not required, proceed to Section 7.3.

7.1.4.1 Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500 mL beaker or Erlenmeyer flask.

7.1.4.2 Add 96.5 mL of reagent water to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use extraction fluid #1. Proceed to Section 7.2.

7.1.4.3 If the pH from Section 7.1.4.2 is >5.0, add 3.5 mL 1N HCl, slurry briefly, cover with a watchglass, heat to 50 °C, and hold at 50 °C for 10 minutes.

7.1.4.4 Let the solution cool to room temperature and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2. Proceed to Section 7.2.

7.1.5 If the aliquot of the waste used for the preliminary evaluation (Sections 7.1.1 - 7.1.4) was determined to be 100% solid at Section 7.1.1.1, then it can be used for the Section 7.2 extraction (assuming at least 100 grams remain), and the Section 7.3 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in Section 7.1.1.7, then another aliquot shall be used for the volatile extraction procedure in Section 7.3. The aliquot of the waste subjected to the procedure in Section 7.1.1.7 might be appropriate for use for the Section 7.2 extraction if an adequate amount of solid (as determined by Section 7.1.1.9) was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to Section 7.2.10 of the nonvolatile TCLP extraction.

7.2 Procedure When Volatiles are not Involved

A minimum sample size of 100 grams (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample (percent solids, See Section 7.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all

of the analyses required. If the amount of extract generated by a single TCLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

7.2.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solid, see Section 7.1.1), weigh out a subsample of the waste (100 gram minimum) and proceed to Section 7.2.9.

7.2.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.2.3 to 7.2.8.

7.2.3 Pre-weigh the container that will receive the filtrate.

7.2.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Section 4.4).

NOTE: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.

7.2.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight. If the waste contains <0.5% dry solids (Section 7.1.2), the liquid portion of the waste, after filtration, is defined as the TCLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the TCLP extract. For wastes containing >0.5% dry solids (Sections 7.1.1 or 7.1.2), use the percent solids information obtained in Section 7.1.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the TCLP extract.

7.2.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the waste is centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.2.7 Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder (see Section 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and

subtract it from the sample weight determined in Section 7.2.5, to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within a 2 minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.2.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (See Section 7.2.12) or stored at 4 °C until time of analysis.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Section 7.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.2.9 If the waste contains <0.5% dry solids (see Section 7.1.2), proceed to Section 7.2.13. If the waste contains >0.5% dry solids (see Section 7.1.1 or 7.1.2), and if particle size reduction of the solid was needed in Section 7.1.3, proceed to Section 7.2.10. If the waste as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Section 7.2.11.

7.2.10 Prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described in Section 7.1.3. When the surface area or particle size has been appropriately altered, quantitatively transfer the solid material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon coated sieve should be used to avoid contamination of the sample.

7.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (Section 7.1.1)} \times \text{weight of waste filtered (Section 7.2.5 or 7.2.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see Section 7.1.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 ± 2 °C during the extraction period.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

7.2.12 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Section 7.2.7. For final filtration of the TCLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed (see Section 4.4) if evaluating the mobility of metals.

7.2.13 Prepare the TCLP extract as follows:

7.2.13.1 If the waste contained no initial liquid phase, the filtered liquid material obtained from Section 7.2.12 is defined as the TCLP extract. Proceed to Section 7.2.14.

7.2.13.2 If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from Section 7.2.12 with the initial liquid phase of the waste obtained in Section 7.2.7. This combined liquid is defined as the TCLP extract. Proceed to Section 7.2.14.

7.2.13.3 If the initial liquid phase of the waste, as obtained from Section 7.2.7, is not or may not be compatible with the filtered liquid resulting from Section 7.2.12, do not combine these liquids. Analyze these liquids, collectively defined as the TCLP extract, and combine the results mathematically, as described in Section 7.2.14.

7.2.14 Following collection of the TCLP extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to

pH <2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4 °C) until analyzed. The TCLP extract shall be prepared and analyzed according to appropriate analytical methods. TCLP extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to ± 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)\ (C_1) + (V_2)\ (C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.2.15 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

7.3 Procedure When Volatiles are Involved

Use the ZHE device to obtain TCLP extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of nonvolatile analytes (e.g., metals, pesticides, etc.).

The ZHE device has approximately a 500 mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a sample from which no additional liquid may be forced out by an applied pressure of 50 psi), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

Do not allow the waste, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any

manipulation of these materials should be done when cold (4 °C) to minimize loss of volatiles.

7.3.1 Pre-weigh the (evacuated) filtrate collection container (See Section 4.6) and set aside. If using a TEDLAR® bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis. The containers listed in Section 4.6 are recommended for use under the conditions stated in Sections 4.6.1 - 4.6.3.

7.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from Section 7.3, Section 7.1.1 and/or 7.1.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

7.3.3 If the waste is 100% solid (see Section 7.1.1), weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to Section 7.3.5.

7.3.4 If the waste contains < 0.5% dry solids (Section 7.1.2), the liquid portion of waste, after filtration, is defined as the TCLP extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For wastes containing ≥ 0.5% dry solids (Sections 7.1.1 and/or 7.1.2), use the percent solids information obtained in Section 7.1.1 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows:

7.3.4.1 For wastes containing < 5% solids (see Section 7.1.1), weigh out a 500 gram subsample of waste and record the weight.

7.3.4.2 For wastes containing ≥ 5% solids (see Section 7.1.1), determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\text{percent solids (Section 7.1.1)}} \times 100$$

Weigh out a subsample of the waste of the appropriate size and record the weight.

7.3.5 If particle size reduction of the solid portion of the waste was required in Section 7.1.3, proceed to Section 7.3.6. If

particle size reduction was not required in Section 7.1.3, proceed to Section 7.3.7.

7.3.6 Prepare the waste for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle size as described in Section 7.1.3. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4 °C prior to particle size reduction. The means used to effect particle size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle size has been appropriately altered, proceed to Section 7.3.7.

7.3.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.

7.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extract collection device to the top plate.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Section 7.3.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to force all headspace slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100% solid (see Section 7.1.1), slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device and proceed to Section 7.3.12.

7.3.9 Attach the evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2 minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.3.10 The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the TCLP extraction as a solid.

If the original waste contained <0.5% dry solids (see Section 7.1.2), this filtrate is defined as the TCLP extract and is analyzed directly. Proceed to Section 7.3.15.

7.3.11 The liquid phase may now be either analyzed immediately (See Sections 7.3.13 through 7.3.15) or stored at 4 °C under minimal headspace conditions until time of analysis. Determine the weight of extraction fluid #1 to add to the ZHE as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (Section 7.1.1)} \times \text{weight of waste filtered (Section 7.3.4 or 7.3.8)}}{100}$$

7.3.12 The following Sections detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #1 is used in all cases (See Section 5.7).

7.3.12.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve,

and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

7.3.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psi and check all ZHE fittings to ensure that they are closed.

7.3.12.3 Place the ZHE in the rotary agitation apparatus (if it is not already there) and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 23 ± 2 °C during agitation.

7.3.13 Following the 18 ± 2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the device is leaking. Check the ZHE for leaking as specified in Section 4.2.1, and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in Section 7.3.9. All extract shall be filtered and collected if the TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase (see Sections 4.6 and 7.3.1).

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured.

7.3.14 If the original waste contained no initial liquid phase, the filtered liquid material obtained from Section 7.3.13 is defined as the TCLP extract. If the waste contained an initial liquid phase, the

filtered liquid material obtained from Section 7.3.13 and the initial liquid phase (Section 7.3.9) are collectively defined as the TCLP extract.

7.3.15 Following collection of the TCLP extract, immediately prepare the extract for analysis and store with minimal headspace at 4 °C until analyzed. Analyze the TCLP extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)\ (C_1) + (V_2)\ (C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phases (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.3.16 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

8.0 QUALITY ASSURANCE

8.1 A minimum of one blank (using the same extraction fluid as used for the samples) must be analyzed for every 20 extractions that have been conducted in an extraction vessel.

8.2 A matrix spike shall be performed for each waste type (e.g., wastewater treatment sludge, contaminated soil, etc.) unless the result exceeds the regulatory level and the data are being used solely to demonstrate that the waste property exceeds the regulatory level. A minimum of one matrix spike must be analyzed for each analytical batch. As a minimum, follow the matrix spike addition guidance provided in each analytical method.

8.2.1 Matrix spikes are to be added after filtration of the TCLP extract and before preservation. Matrix spikes should not be added prior to TCLP extraction of the sample.

8.2.2 In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration, but may not be not less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be

added to the same nominal volume of TCLP extract as that which was analyzed for the unspiked sample.

8.2.3 The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist. Use of other internal calibration methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the analyte concentration in the TCLP extract when the recovery of the matrix spike is below the expected analytical method performance.

8.2.4 Matrix spike recoveries are calculated by the following formula:

$$\%R\ (\%Recovery) = 100\ (X_s - X_u)/K$$

where:
X_s = measured value for the spiked sample,
X_u = measured value for the unspiked sample, and
K = known value of the spike in the sample.

8.3 All quality control measures described in the appropriate analytical methods shall be followed.

8.4 The use of internal calibration quantitation methods shall be employed for a metallic contaminant if: (1) Recovery of the contaminant from the TCLP extract is not at least 50% and the concentration does not exceed the regulatory level, and (2) The concentration of the contaminant measured in the extract is within 20% of the appropriate regulatory level.

8.4.1. The method of standard additions shall be employed as the internal calibration quantitation method for each metallic contaminant.

8.4.2 The method of standard additions requires preparing calibration standards in the sample matrix rather than reagent water or blank solution. It requires taking four identical aliquots of the solution and adding known amounts of standard to three of these aliquots. The forth aliquot is the unknown. Preferably, the first addition should be prepared so that the resulting concentration is approximately 50% of the expected concentration of the sample. The second and third additions should be prepared so that the concentrations are approximately 100% and 150% of the expected concentration of the sample. All four aliquots are maintained at the same final volume by adding reagent water or a blank solution, and may need dilution adjustment to maintain the signals in the linear range of the instrument technique. All four aliquots are analyzed.

8.4.3 Prepare a plot, or subject data to linear regression, of instrument signals or external-calibration-derived concentrations as the dependant variable (y-axis) versus concentrations of the additions of standard as the independent variable (x-axis). Solve for the intercept of

the abscissa (the independent variable, x-axis) which is the concentration in the unknown.

8.4.4 Alternately, subtract the instrumental signal or external-calibration-derived concentration of the unknown (unspiked) sample from the instrumental signals or external-calibration-derived concentrations of the standard additions. Plot or subject to linear regression of the corrected instrument signals or external-calibration-derived concentrations as the dependant variable versus the independent variable. Derive concentrations for unknowns using the internal calibration curve as if it were an external calibration curve.

8.5 Samples must undergo TCLP extraction within the following time periods:

SAMPLE MAXIMUM HOLDING TIMES [Days]				
	From: Field collection To: TCLP extraction	From: TCLP extraction To: Preparative extraction	From: Preparative extraction To: Determinative analysis	Total elapsed time
Volatiles	14	NA	14	28
Semi-volatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360

NA = Not applicable

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

9.0 METHOD PERFORMANCE

9.1 Ruggedness. Two ruggedness studies have been performed to determine the effect of various perturbations on specific elements of the TCLP protocol. Ruggedness testing determines the sensitivity of small procedural variations which might be expected to occur during routine laboratory application.

9.1.1 Metals - The following conditions were used when leaching a waste for metals analysis:

Varying Conditions	
Liquid/Solid ratio	19:1 vs. 21:1
Extraction time	16 hours vs. 18 hours
Headspace	20% vs. 60%
Buffer #2 acidity	190 meq vs. 210 meq
Acid-washed filters	yes vs. no
Filter type	0.7 μm glass fiber vs. 0.45 μm vs. polycarbonate
Bottle type	borosilicate vs. flint glass

Of the seven method variations examined, acidity of the extraction fluid had the greatest impact on the results. Four of 13 metals from an API separator sludge/electroplating waste (API/EW) mixture and two of three metals from an ammonia lime still bottom waste were extracted at higher levels by the more acidic buffer. Because of the sensitivity to pH changes, the method requires that the extraction fluids be prepared so that the final pH is within ± 0.05 units as specified.

9.1.2 Volatile Organic Compounds - The following conditions were used when leaching a waste for VOC analysis:

Varying Conditions	
Liquid/Solid ratio	19:1 vs. 21:1
Headspace	0% vs. 5%
Buffer #1 acidity	60 meq vs. 80 meq
Method of storing extract	Syringe vs. Tedlar® bag
Aliquotting	yes vs. no
Pressure behind piston	0 psi vs. 20 psi

None of the parameters had a significant effect on the results of the ruggedness test.

9.2 Precision. Many TCLP precision (reproducibility) studies have been performed, and have shown that, in general, the precision of the TCLP is comparable to or exceeds that of the EP toxicity test and that method precision is adequate. One of the more significant contributions to poor precision appears to be related to sample homogeneity and inter-laboratory variation (due to the nature of waste materials).

9.2.1 Metals - The results of a multi-laboratory study are shown in Table 6, and indicate that a single analysis of a waste may not be adequate for waste characterization and identification requirements.

9.2.2 Semi-Volatile Organic Compounds - The results of two studies are shown in Tables 7 and 8. Single laboratory precision was excellent with greater than 90 percent of the results exhibiting an RSD less than 25 percent. Over 85 percent of all individual compounds in the multi-laboratory study fell in the RSD range of 20 - 120 percent. Both studies concluded that the TCLP provides adequate precision. It was also determined that the high acetate content of the extraction fluid did not present problems (i.e., column degradation of the gas chromatograph) for the analytical conditions used.

9.2.3 Volatile Organic Compounds - Eleven laboratories participated in a collaborative study of the use of the ZHE with two waste types which were fortified with a mixture of VOCs. The results of the collaborative study are shown in Table 9. Precision results for VOCs tend to occur over a considerable range. However, the range and mean RSD compared very closely to the same collaborative study metals results in Table 6. Blackburn and Show concluded that at the 95% level of significance: 1) recoveries among laboratories were statistically similar, 2) recoveries did not vary significantly between the two sample types, and 3) each laboratory showed the same pattern of recovery for each of the two samples.

10.0 REFERENCES

1. Blackburn, W.B. and Show, I. "Collaborative Study of the Toxicity Characteristics Leaching Procedure (TCLP)." Draft Final Report, Contract No. 68-03-1958, S-Cubed, November 1986.

2. Newcomer, L.R., Blackburn, W.B., Kimmell, T.A. "Performance of the Toxicity Characteristic Leaching Procedure." Wilson Laboratories, S-Cubed, U.S. EPA, December 1986.

3. Williams, L.R., Francis, C.W.; Maskarinec, M.P., Taylor D.R., and Rothman, N. "Single-Laboratory Evaluation of Mobility Procedure for Solid Waste." EMSL, ORNL, S-Cubed, ENSECO.

Table 1.
Volatile Analytes[1,2]

Compound	CAS No.
Acetone	67-64-1
Benzene	71-43-2
n-Butyl alcohol	71-36-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1,-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

[1] When testing for any or all of these analytes, the zero-headspace extractor vessel shall be used instead of the bottle extractor.

[2] Benzene, carbon tetrachloride, chlorobenzene, chloroform, 1,2-dichloroethane, 1,1-dichloroethylene, methyl ethyl ketone, tetrachloroethylene, and vinyl chloride are toxicity characteristic constituents.

Table 2.
Suitable Rotary Agitation Apparatus[1]

Company	Location	Model No.
Analytical Testing and Consulting Services, Inc.	Warrington, PA (215) 343-4490	4-vessel extractor (DC20S) 8-vessel extractor (DC20) 12-vessel extractor (DC20B) 24-vessel extractor (DC24C)
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	2-vessel (3740-2-BRE) 4-vessel (3740-4-BRE) 6-vessel (3740-6-BRE) 8-vessel (3740-8-BRE) 12-vessel (3740-12-BRE) 24-vessel (3740-24-BRE)
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	8-vessel (08-00-00) 4-vessel (04-00-00)
IRA Machine Shop and Laboratory	Santurce, PR (809) 752-4004	8-vessel (011001)
Lars Lande Manufacturing	Whitmore Lake, MI (313) 449-4116	10-vessel (10VRE) 5-vessel (5VRE) 6-vessel (6VRE)
Millipore Corp.	Bedford, MA (800) 225-3384	4-ZHE or 4 2-liter bottle extractor (YT310RAHW)

[1] Any device that rotates the extraction vessel in an end-over-end fashion at 30 ± 2 rpm is acceptable.

Table 3.
Suitable Zero-Headspace Extractor Vessels[1]

Company	Location	Model No.
Analytical Testing & Consulting Services, Inc.	Warrington, PA (215) 343-4490	C102, Mechanical Pressure Device
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	3745-ZHE, Gas Pressure Device
Lars Lande Manufacturing[2]	Whitmore Lake, MI (313) 449-4116	ZHE-11, Gas Pressure Device
Millipore Corporation	Bedford, MA (800) 225-3384	YT30090HW, Gas Pressure Device
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	VOLA-TOX1, Gas Pressure Device
Gelman Science	Ann Arbor, MI (800) 521-1520	15400 Gas Pressure Device

[1] Any device that meets the specifications listed in Section 4.2.1 of the method is suitable.

[2] This device uses a 110 mm filter.

Table 4.
Suitable Filter Holders[1]

Company	Location	Model/ Catalogue No.	Size
Nucleopore Corporation	Pleasanton, CA (800) 882-7711	425910 410400	142 mm 47 mm
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	302400 311400	142 mm 47 mm
Millipore Corporation	Bedford, MA (800) 225-3384	YT30142HW XX1004700	142 mm 47 mm

[1] Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic analytes are of concern. The 142 mm size filter holder is recommended.

Table 5.
Suitable Filter Media[1]

Company	Location	Model	Pore Size (μm)
Millipore Corporation	Bedford, MA (800) 225-3384	AP40	0.7
Nucleopore Corporation	Pleasanton, CA (415) 463-2530	211625	0.7
Whatman Laboratory Products, Inc.	Clifton, NJ (201) 773-5800	GFF	0.7
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	GF75	0.7
Gelman Science	Ann Arbor, MI (800) 521-1520	66256 (90mm) 66257 (142mm)	0.7

[1] Any filter that meets the specifications in Section 4.4 of the Method is suitable.

Table 6. Multi-Laboratory TCLP Metals, Precision

Waste	Extraction Fluid	Metal	$\bar{X}$	S	%RSD
Ammonia Lime Still Bottoms	#1	Cadmium	0.053	0.031	60
	#2		0.023	0.017	76
	#1	Chromium	0.015	0.0014	93
	#2		0.0032	0.0037	118
	#1	Lead	0.0030	0.0027	90
	#2		0.0032	0.0028	87
API/EW Mixture	#1	Cadmium	0.0046	0.0028	61
	#2		0.0005	0.0004	77
	#1	Chromium	0.0561	0.0227	40
	#2		0.105	0.018	17
	#1	Lead	0.0031	0.0031	100
	#2		0.0124	0.0136	110
Fossil Fuel Fly Ash	#1	Cadmium	0.080	0.069	86
	#2		0.093	0.067	72
	#1	Chromium	0.017	0.014	85
	#2		0.070	0.040	57
	#1	Lead	0.0087	0.0074	85
	#2		0.0457	0.0083	18
				%RSD Range = 17 - 118 Mean %RSD = 74	

NOTE: $\bar{X}$ = Mean results from 6 - 12 different laboratories
Units = mg/L
Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

Table 7. Single-Laboratory Semi-Volatiles, Precision

Waste	Compound	Extraction Fluid	$\bar{X}$	S	%RSD
Ammonia Lime Still Bottoms	Phenol	#1	19000	2230	11.6
		#2	19400	929	4.8
	2-Methylphenol	#1	2000	297	14.9
		#2	1860	52.9	2.8
	4-Methylphenol	#1	7940	1380	17.4
		#2	7490	200	2.7
	2,4-Dimethylphenol	#1	321	46.8	14.6
		#2	307	45.8	14.9
	Naphthalene	#1	3920	413	10.5
		#2	3827	176	4.6
	2-Methylnaphthalene	#1	290	44.8	15.5
		#2	273	19.3	7.1
	Dibenzofuran	#1	187	22.7	12.1
		#2	187	7.2	3.9
	Acenaphthylene	#1	703	89.2	12.7
		#2	663	20.1	3.0
	Fluorene	#1	151	17.6	11.7
		#2	156	2.1	1.3
	Phenanthrene	#1	241	22.7	9.4
		#2	243	7.9	3.3
	Anthracene	#1	33.2	6.19	18.6
		#2	34.6	1.55	4.5
	Fluoranthrene	#1	25.3	1.8	7.1
		#2	26.0	1.8	7.1
API/EW Mixture	Phenol	#1	40.7	13.5	33.0
		#2	19.0	1.76	9.3
	2,4-Dimethylphenol	#1	33.0	9.35	28.3
		#2	43.3	8.61	19.9
	Naphthalene	#1	185	29.4	15.8
		#2	165	24.8	15.0
	2-Methylnaphthalene	#1	265	61.2	23.1
		#2	200	18.9	9.5
				%RSD Range = 1 - 33 Mean %RSD = 12	

NOTE: Units = µg/L
Extractions were performed in triplicate
All results were at least 2x the detection limit
Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

Table 8. Multi-Laboratory Semi-Volatiles, Precision

Waste	Compound	Extraction Fluid	$\bar{X}$	S	%RSD
Ammonia Lime	BNAs	#1	10043	7680	76.5
Still Bottoms (A)		#2	10376	6552	63.1
API/EW	BNAs	#1	1624	675	41.6
Mixture (B)		#2	2074	1463	70.5
Fossil Fuel	BNAs	#1	750	175	23.4
Fly Ash (C)		#2	739	342	46.3
					Mean %RSD = 54

NOTE: Units = µg/L
$\bar{X}$ = Mean results from 3 - 10 labs
Extraction Fluid #1 = pH 4.9
#2 = pH 2.9

%RSD Range for Individual Compounds

A, #1	0 - 113
A, #2	28 - 108
B, #1	20 - 156
B, #2	49 - 128
C, #1	36 - 143
C, #2	61 - 164

Table 9. Multi-Laboratory (11 Labs) VOCs, Precision

Waste	Compound	$\bar{X}$	S	%RSD
Mine Tailings	Vinyl chloride	6.36	6.36	100
	Methylene chloride	12.1	11.8	98
	Carbon disulfide	5.57	2.83	51
	1,1-Dichloroethene	21.9	27.7	127
	1,1-Dichloroethane	31.4	25.4	81
	Chloroform	46.6	29.2	63
	1,2-Dichloroethane	47.8	33.6	70
	2-Butanone	43.5	36.9	85
	1,1,1-Trichloroethane	20.9	20.9	100
	Carbon tetrachloride	12.0	8.2	68
	Trichloroethene	24.7	21.2	86
	1,1,2-Trichloroethene	19.6	10.9	56
	Benzene	37.9	28.7	76
	1,1,2,2-Tetrachloroethane	34.9	25.6	73
	Toluene	29.3	11.2	38
	Chlorobenzene	35.6	19.3	54
	Ethylbenzene	4.27	2.80	66
	Trichlorofluoromethane	3.82	4.40	115
	Acrylonitrile	76.7	110.8	144
Ammonia Lime Still Bottoms	Vinyl chloride	5.00	4.71	94
	Methylene chloride	14.3	13.1	92
	Carbon disulfide	3.37	2.07	61
	1,1-Dichloroethene	52.1	38.8	75
	1,1-Dichloroethane	52.8	25.6	49
	Chloroform	64.7	28.4	44
	1,2-Dichloroethane	43.1	31.5	73
	2-Butanone	59.0	39.6	67
	1,1,1-Trichloroethane	53.6	40.9	76
	Carbon tetrachloride	7.10	6.1	86
	Trichloroethene	57.3	34.2	60
	1,1,2-Trichloroethene	6.7	4.7	70
	Benzene	61.3	26.8	44
	1,1,2,2-Tetrachloroethane	3.16	2.1	66
	Toluene	69.0	18.5	27
	Chlorobenzene	71.8	12.0	17
	Ethylbenzene	3.70	2.2	58
	Trichlorofluoromethane	4.05	4.8	119
	Acrylonitrile	29.4	34.8	118
			%RSD Range = 17 - 144 Mean %RSD = 75	

NOTE: Units = μg/L

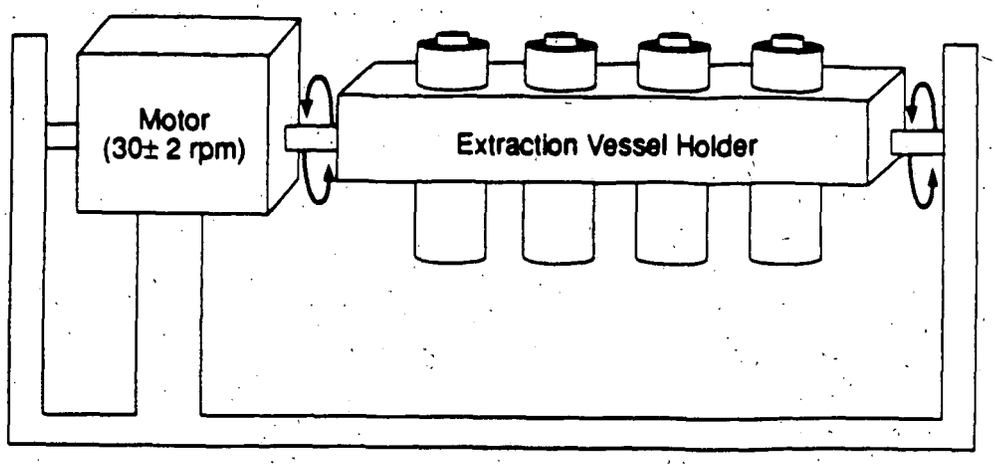


Figure 1. Rotary Agitation Apparatus

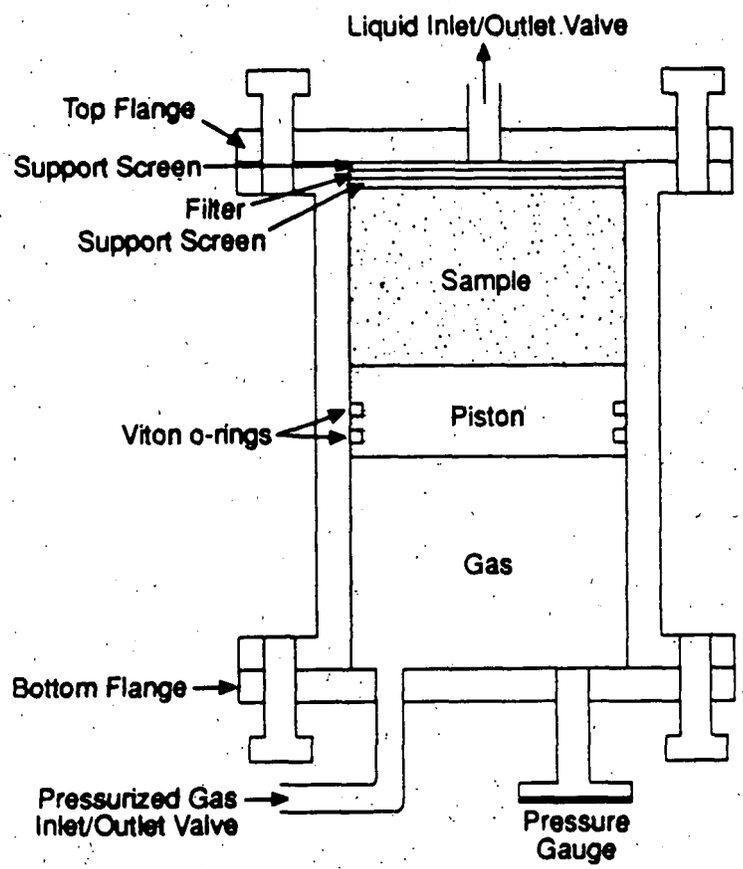
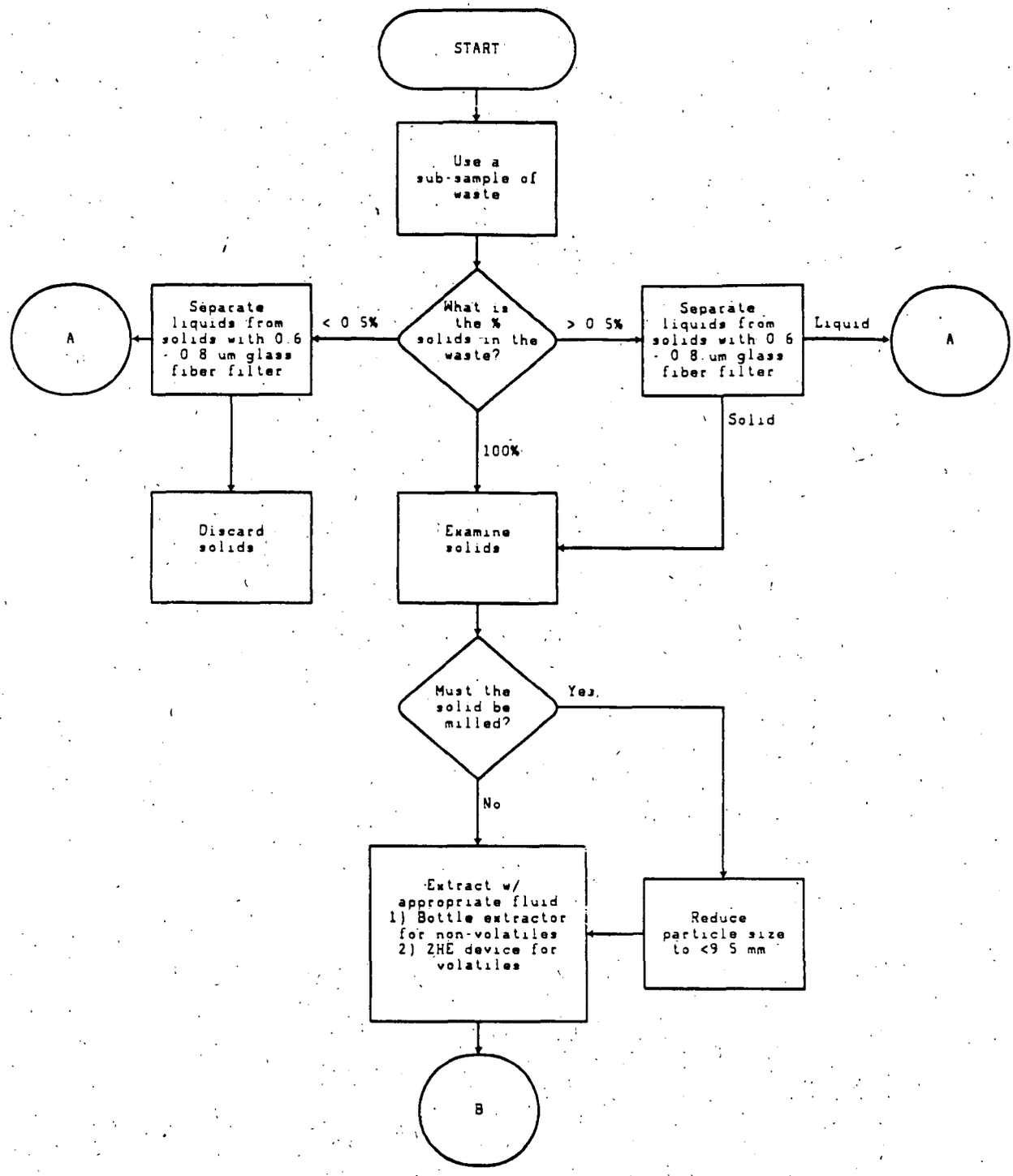


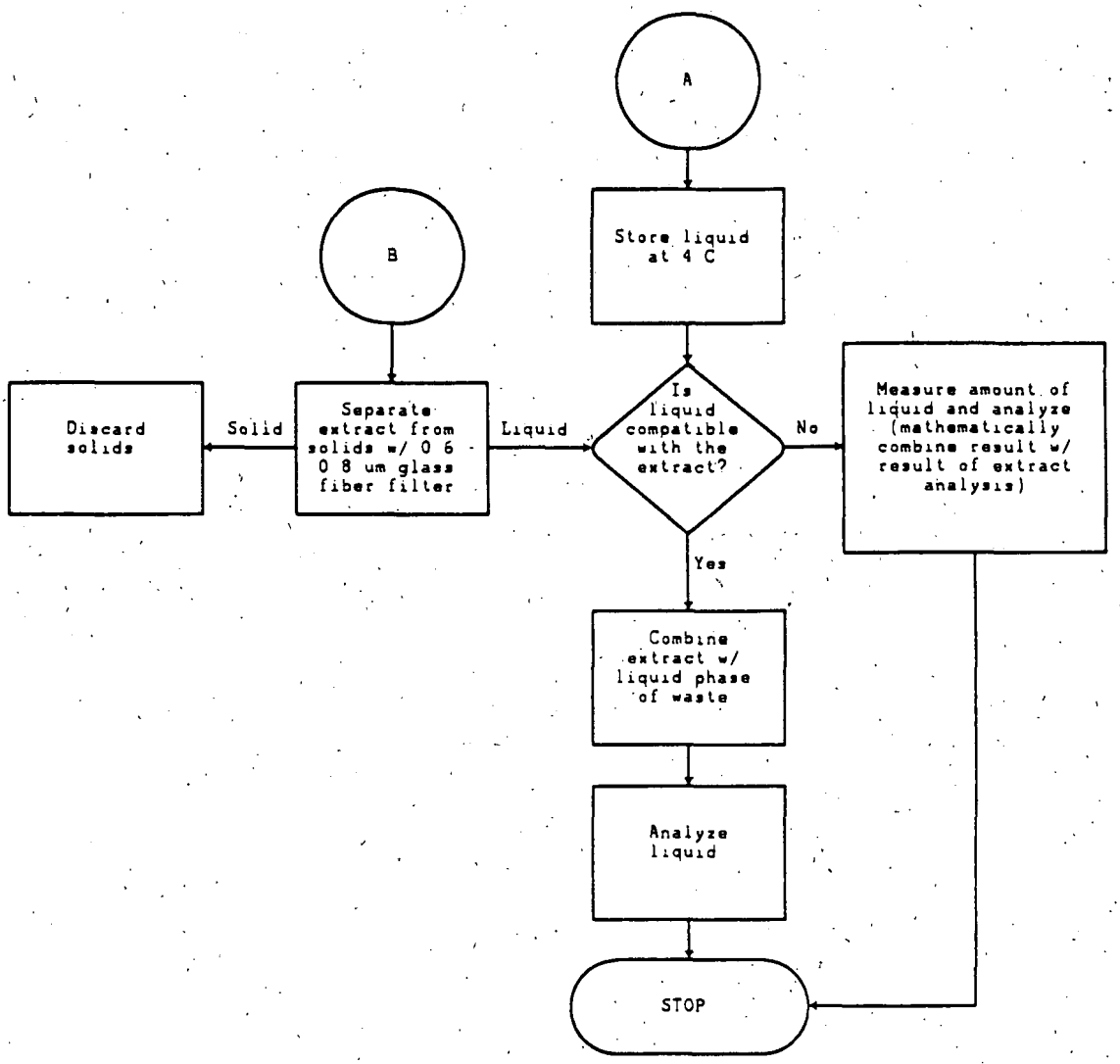
Figure 2. Zero-Headspace Extractor (ZHE)

METHOD 1311

TOXICITY CHARACTERISTIC LEACHATE PROCEDURE



TOXICITY CHARACTERISTIC LEACHATE PROCEDURE



METHOD 1312

SYNTHETIC PRECIPITATION LEACHING PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 Method 1312 is designed to determine the mobility of both organic and inorganic analytes present in liquids, soils, and wastes.

2.0 SUMMARY OF METHOD

2.1 For liquid samples (i.e., those containing less than 0.5 % dry solid material), the sample, after filtration through a 0.6 to 0.8 μm glass fiber filter, is defined as the 1312 extract.

2.2 For samples containing greater than 0.5 % solids, the liquid phase, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the region of the country where the sample site is located if the sample is a soil. If the sample is a waste or wastewater, the extraction fluid employed is a pH 4.2 solution. A special extractor vessel is used when testing for volatile analytes (see Table 1 for a list of volatile compounds). Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 μm glass fiber filter.

2.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 1) at 30 $\pm$ 2 rpm. Suitable devices known to EPA are identified in Table 2.

4.2 Extraction Vessels

4.2.1 Zero Headspace Extraction Vessel (ZHE). This device is for use only when the sample is being tested for the mobility of volatile analytes (i.e., those listed in Table 1). The ZHE (depicted in Figure 2) allows for liquid/solid separation within the device and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the

vessel (see Step 4.3.1). These vessels shall have an internal volume of 500-600 mL and be equipped to accommodate a 90-110 mm filter. The devices contain VITON®[1] O-rings which should be replaced frequently. Suitable ZHE devices known to EPA are identified in Table 3.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psig or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for 1312 analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psig, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psig, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedure (see Step 7.3) refers to pounds-per-square-inch (psig), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

4.2.2 Bottle Extraction Vessel. When the sample is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste (see Step 4.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Step 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.3 Filtration Devices: It is recommended that all filtrations be performed in a hood.

4.3.1 Zero-Headspace Extraction Vessel (ZHE): When the sample is evaluated for volatiles, the zero-headspace extraction vessel described in Step 4.2.1 is used for filtration. The device shall be capable of

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[1]VITON® is a trademark of Du Pont.

supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psig).

NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.3.2 Filter Holder: When the sample is evaluated for other than volatile analytes, a filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psig or more. The type of filter holder used depends on the properties of the material to be filtered (see Step 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (<10 %) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration. Suitable filter holders known to EPA are listed in Table 4.

4.3.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb sample components of interest. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high-density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) may be used only when evaluating the mobility of metals. Borosilicate glass bottles are recommended for use over other types of glass bottles, especially when inorganics are analytes of concern.

4.4 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8-μm . Filters known to EPA which meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with reagent water (a minimum of 1-L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters: The meter should be accurate to $\pm$ 0.05 units at 25°C.

4.6 ZHE Extract Collection Devices: TEDLAR®[2] bags or glass, stainless steel or PTFE gas-tight syringes are used to collect the initial liquid phase and the final extract when using the ZHE device. These devices listed are recommended for use under the following conditions:

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., <1 % of

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[2]TEDLAR® is a registered trademark of Du Pont.

total waste), the TEDLAR® bag or a 600 mL syringe should be used to collect and combine the initial liquid and solid extract.

4.6.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., >1 % of total waste), the syringe or the TEDLAR® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100 % solid) or has no significant solid phase (is <0.5% solid) , either the TEDLAR® bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g., a positive displacement or peristaltic pump, a gas-tight syringe, pressure filtration unit (see Step 4.3.2), or other ZHE device).

4.8 Laboratory Balance: Any laboratory balance accurate to within ± 0.01 grams may be used (all weight measurements are to be within ± 0.1 grams).

4.9 Beaker or Erlenmeyer flask, glass, 500 mL.

4.10 Watchglass, appropriate diameter to cover beaker or Erlenmeyer flask.

4.11 Magnetic stirrer.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water is defined as water in which an interferant is not observed at or above the method's detection limit of the analyte(s) of interest. For nonvolatile extractions, ASTM Type II water or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.2.1 Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing about 500 grams of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.2.2 A water purification system (Millipore Super-Q or equivalent) may also be used to generate reagent water for volatile extractions.

5.2.3 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at 90 ± 5 degrees C, bubble a contaminant-free inert gas (e.g. nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow mouth screw-cap bottle under zero-headspace and seal with a Teflon-lined septum and cap.

5.3 Sulfuric acid/nitric acid (60/40 weight percent mixture) H_2SO_4/HNO_3. Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid. If preferred, a more dilute H_2SO_4/HNO_3 acid mixture may be prepared and used in steps 5.4.1 and 5.4.2 making it easier to adjust the pH of the extraction fluids.

5.4 Extraction fluids.

5.4.1 Extraction fluid #1: This fluid is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids (or a suitable dilution) to reagent water (Step 5.2) until the pH is 4.20 ± 0.05. The fluid is used to determine the leachability of soil from a site that is east of the Mississippi River, and the leachability of wastes and wastewaters.

NOTE: Solutions are unbuffered and exact pH may not be attained.

5.4.2 Extraction fluid #2: This fluid is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids (or a suitable dilution) to reagent water (Step 5.2) until the pH is 5.00 ± 0.05. The fluid is used to determine the leachability of soil from a site that is west of the Mississippi River.

5.4.3 Extraction fluid #3: This fluid is reagent water (Step 5.2) and is used to determine cyanide and volatiles leachability.

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

5.5 Analytical standards shall be prepared according to the appropriate analytical method.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples shall be collected using an appropriate sampling plan.

6.2 There may be requirements on the minimal size of the field sample depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for the preliminary evaluations of the percent

solids and the particle size. An aliquot may be needed to conduct the nonvolatile analyte extraction procedure. If volatile organics are of concern, another aliquot may be needed. Quality control measures may require additional aliquots. Further, it is always wise to collect more sample just in case something goes wrong with the initial attempt to conduct the test.

6.3 Preservatives shall not be added to samples before extraction.

6.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.5 When the sample is to be evaluated for volatile analytes, care shall be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon-lined septum capped vials and stored at 4°C. Samples should be opened only immediately prior to extraction).

6.6 1312 extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs (see Step 7.2.14 if precipitation occurs). Extracts should be preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for organic analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See Step 8.0 (Quality Control) for acceptable sample and extract holding times.

7.0 PROCEDURE

7.1 Preliminary Evaluations

Perform preliminary 1312 evaluations on a minimum 100 gram aliquot of sample. This aliquot may not actually undergo 1312 extraction. These preliminary evaluations include: (1) determination of the percent solids (Step 7.1.1); (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (Step 7.1.2); and (3) determination of whether the solid portion of the waste requires particle size reduction (Step 7.1.3).

7.1.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1.1 If the sample will obviously yield no free liquid when subjected to pressure filtration (i.e., is 100% solid), weigh out a representative subsample (100 g minimum) and proceed to Step 7.1.3.

7.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device

discussed in Step 4.3.2, and is outlined in Steps 7.1.1.3 through 7.1.1.9.

7.1.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.1.4 Assemble filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.1.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight.

7.1.1.6 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.1.1.7 Quantitatively transfer the sample to the filter holder (liquid and solid phases). Spread the sample evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

Gradually apply vacuum or gentle pressure of 1-10 psig, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psig, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10 psig increments to a maximum of 50 psig. After each incremental increase of 10 psig, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psig increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psig (i.e., filtration does not result in any additional filtrate within any 2-minute period), stop the filtration.

NOTE: If sample material (>1 % of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.1.1.5 to determine the weight of the sample that will be filtered.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.1.8 The material in the filter holder is defined as the solid phase of the sample, and the filtrate is defined as the liquid phase.

NOTE: Some samples, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid, but even after applying vacuum or pressure filtration, as outlined in Step 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.1.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Step 7.1.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the sample by subtracting the weight of the liquid phase from the weight of the total sample, as determined in Step 7.1.1.5 or 7.1.1.7.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (Step 7.1.1.9)}}{\text{Total weight of waste (Step 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2 If the percent solids determined in Step 7.1.1.9 is equal to or greater than 0.5%, then proceed either to Step 7.1.3 to determine whether the solid material requires particle size reduction or to Step 7.1.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined in Step 7.1.1.9 is less than 0.5%, then proceed to Step 7.2.9 if the nonvolatile 1312 analysis is to be performed, and to Step 7.3 with a fresh portion of the waste if the volatile 1312 analysis is to be performed.

7.1.2.1 Remove the solid phase and filter from the filtration apparatus.

7.1.2.2 Dry the filter and solid phase at 100 ± 20°C until two successive weighings yield the same value within ± 1 %. Record the final weight.

Caution: The drying oven should be vented to a hood or other appropriate device to eliminate the possibility of fumes from the sample escaping into the laboratory. Care should be taken to ensure that the sample will not flash or violently react upon heating.

7.1.2.3 Calculate the percent dry solids as follows:

$$\text{Percent dry solids} = \frac{\text{(Weight of dry sample + filter) - tared weight of filter}}{\text{Initial weight of sample (Step 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2.4 If the percent dry solids is less than 0.5%, then proceed to Step 7.2.9 if the nonvolatile 1312 analysis is to be performed, and to Step 7.3 if the volatile 1312 analysis is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile 1312 analysis is to be performed, return to the beginning of this Step (7.1) and, with a fresh portion of sample, determine whether particle size reduction is necessary (Step 7.1.3).

7.1.3 Determination of whether the sample requires particle-size reduction (particle-size is reduced during this step): Using the solid portion of the sample, evaluate the solid for particle size. Particle-size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see Step 7.3.6).

NOTE: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample-specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

7.1.4 Determination of appropriate extraction fluid:

7.1.4.1 For soils, if the sample is from a site that is east of the Mississippi River, extraction fluid #1 should be used. If the sample is from a site that is west of the Mississippi River, extraction fluid #2 should be used.

7.1.4.2 For wastes and wastewater, extraction fluid #1 should be used.

7.1.4.3 For cyanide-containing wastes and/or soils, extraction fluid #3 (reagent water) must be used because leaching of cyanide-containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

7.1.5 If the aliquot of the sample used for the preliminary evaluation (Steps 7.1.1 - 7.1.4) was determined to be 100% solid at Step 7.1.1.1, then it can be used for the Step 7.2 extraction (assuming at least 100 grams remain), and the Step 7.3 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in Step 7.1.1.7, then another aliquot shall be used for the volatile extraction procedure in Step 7.3. The aliquot of the waste subjected to the procedure in Step 7.1.1.7 might be appropriate for use for the Step 7.2 extraction if an adequate amount of solid (as determined by Step 7.1.1.9)

was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to Step 7.2.10 of the nonvolatile 1312 extraction.

7.2 Procedure When Volatiles Are Not Involved

A minimum sample size of 100 grams (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample (percent solids, See Step 7.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of 1312 extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single 1312 extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

7.2.1 If the sample will obviously yield no liquid when subjected to pressure filtration (i.e., is 100 % solid, see Step 7.1.1), weigh out a subsample of the sample (100 gram minimum) and proceed to Step 7.2.9.

7.2.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in Step 4.3.2 and is outlined in Steps 7.2.3 to 7.2.8.

7.2.3 Pre-weigh the container that will receive the filtrate.

7.2.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Step 4.4).

NOTE: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.

7.2.5 Weigh out a subsample of the sample (100 gram minimum) and record the weight. If the waste contains <0.5 % dry solids (Step 7.1.2), the liquid portion of the waste, after filtration, is defined as the 1312 extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the 1312 extract. For wastes containing >0.5 % dry solids (Steps 7.1.1 or 7.1.2), use the percent solids information obtained in Step 7.1.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the 1312 extract.

7.2.6 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the sample is centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.2.7 Quantitatively transfer the sample (liquid and solid phases) to the filter holder (see Step 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

Gradually apply vacuum or gentle pressure of 1-10 psig, until air or pressurizing gas moves through the filter. If this point if not reached under 10 psig, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10-psig increments to maximum of 50 psig. After each incremental increase of 10 psig, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psig increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psig (i.e., filtration does not result in any additional filtrate within a 2-minute period), stop the filtration.

NOTE: If waste material (>1 % of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.2.5, to determine the weight of the waste sample that will be filtered.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.2.8 The material in the filter holder is defined as the solid phase of the sample, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (see Step 7.2.12) or stored at 4°C until time of analysis.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material which appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Step 7.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid, and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.2.9 If the sample contains <0.5% dry solids (see Step 7.1.2), proceed to Step 7.2.13. If the sample contains >0.5 % dry solids (see Step 7.1.1 or 7.1.2), and if particle-size reduction of the solid was needed in Step 7.1.3, proceed to Step 7.2.10. If the sample as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Step 7.2.11.

7.2.10 Prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the waste to a surface area or particle-size as described in Step 7.1.3. When the surface area or particle-size has been appropriately altered, quantitatively transfer the solid material

into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon-coated sieve should be used to avoid contamination of the sample.

7.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{\% solids (Step 7.1.1)} \times \text{weight of waste filtered (Step 7.2.5 or 7.2.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see Step 7.1.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary extractor device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 ± 2°C during the extraction period.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of sample (e.g., limed or calcium carbonate-containing sample may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

7.2.12 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Step 7.2.7. For final filtration of the 1312 extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed (see Step 4.4) if evaluating the mobility of metals.

7.2.13 Prepare the 1312 extract as follows:

7.2.13.1 If the sample contained no initial liquid phase, the filtered liquid material obtained from Step 7.2.12 is defined as the 1312 extract. Proceed to Step 7.2.14.

7.2.13.2 If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from Step 7.2.12 with the initial liquid phase of the sample obtained in Step 7.2.7. This combined liquid is defined as the 1312 extract. Proceed to Step 7.2.14.

7.2.13.3 If the initial liquid phase of the waste, as obtained from Step 7.2.7, is not or may not be compatible with the filtered liquid resulting from Step 7.2.12, do not combine these

liquids. Analyze these liquids, collectively defined as the 1312 extract, and combine the results mathematically, as described in Step 7.2.14.

7.2.14 Following collection of the 1312 extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to pH < 2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4°C) until analyzed. The 1312 extract shall be prepared and analyzed according to appropriate analytical methods. 1312 extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to ± 0.5 %), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)\ (C_1) + (V_2)\ (C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.2.15 Compare the analyte concentrations in the 1312 extract with the levels identified in the appropriate regulations. Refer to Section 8.0 for quality assurance requirements.

7.3 Procedure When Volatiles Are Involved

Use the ZHE device to obtain 1312 extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of non-volatile analytes (e.g., metals, pesticides, etc.).

The ZHE device has approximately a 500 mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a sample from which no additional liquid may be forced out by an applied pressure of 50 psig), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

Do not allow the sample, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (4°C) to minimize loss of volatiles.

7.3.1 Pre-weigh the (evacuated) filtrate collection container (see Step 4.6) and set aside. If using a TEDLAR® bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis. The containers listed in Step 4.6 are recommended for use under the conditions stated in Steps 4.6.1-4.6.3.

7.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from Step 7.3, Step 7.1.1 and/or 7.1.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

7.3.3 If the sample is 100% solid (see Step 7.1.1), weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to Step 7.3.5.

7.3.4 If the sample contains <0.5% dry solids (Step 7.1.2), the liquid portion of waste, after filtration, is defined as the 1312 extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For samples containing ≥0.5% dry solids (Steps 7.1.1 and/or 7.1.2), use the percent solids information obtained in Step 7.1.1 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows:

7.3.4.1 For samples containing <5% solids (see Step 7.1.1), weigh out a 500 gram subsample of waste and record the weight.

7.3.4.2 For wastes containing >5% solids (see Step 7.1.1), determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\text{percent solids (Step 7.1.1)}} \times 100$$

Weigh out a subsample of the waste of the appropriate size and record the weight.

7.3.5 If particle-size reduction of the solid portion of the sample was required in Step 7.1.3, proceed to Step 7.3.6. If particle-size reduction was not required in Step 7.1.3, proceed to Step 7.3.7.

7.3.6 Prepare the sample for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle size as described in Step 7.1.3.1. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4°C prior to particle-size reduction. The means used to effect particle-size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

> NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle-size has been appropriately altered, proceed to Step 7.3.7.

7.3.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge samples prior to filtration.

7.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens into the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extraction collection device to the top plate.

> Note: If sample material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Step 7.3.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psig (or more if necessary) to force all headspace slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100 % solid (see Step 7.1.1), slowly increase the pressure to a maximum of 50 psig to force most of the headspace out of the device and proceed to Step 7.3.12.

7.3.9 Attach the evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psig to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10-psig increments to a maximum of 50 psig. After each incremental increase of 10 psig, if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psig increment. When liquid flow has ceased such that continued pressure filtration at 50 psig does not result in any additional filtrate within a 2-minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.3.10 The material in the ZHE is defined as the solid phase of the sample and the filtrate is defined as the liquid phase.

NOTE: Some samples, such as oily wastes and some paint wastes, will obviously contain some material which appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid, and is carried through the 1312 extraction as a solid.

If the original waste contained <0.5 % dry solids (see Step 7.1.2), this filtrate is defined as the 1312 extract and is analyzed directly. Proceed to Step 7.3.15.

7.3.11 The liquid phase may now be either analyzed immediately (see Steps 7.3.13 through 7.3.15) or stored at 4°C under minimal headspace conditions until time of analysis. Determine the weight of extraction fluid #3 to add to the ZHE as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{\% solids (Step 7.1.1)} \times \text{weight of waste filtered (Step 7.3.4 or 7.3.8)}}{100}$$

7.3.12 The following steps detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #3 is used in all cases (see Step 5.4.3).

7.3.12.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into

the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

7.3.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psig (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psig and check all ZHE fittings to ensure that they are closed.

7.3.12.3 Place the ZHE in the rotary extractor apparatus (if it is not already there) and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 23 ± 2°C during agitation.

7.3.13 Following the 18 ± 2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the ZHE is leaking. Check the ZHE for leaking as specified in Step 4.2.1, and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in Step 7.3.9. All extracts shall be filtered and collected if the TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase (see Steps 4.6 and 7.3.1).

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured

7.3.14 If the original sample contained no initial liquid phase, the filtered liquid material obtained from Step 7.3.13 is defined as the 1312 extract. If the sample contained an initial liquid phase, the filtered liquid material obtained from Step 7.3.13 and the initial liquid phase (Step 7.3.9) are collectively defined as the 1312 extract.

7.3.15 Following collection of the 1312 extract, immediately prepare the extract for analysis and store with minimal headspace at 4°C

until analyzed. Analyze the 1312 extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume- weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)\ (C_1) + (V_2)\ (C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phases (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.3.16 Compare the analyte concentrations in the 1312 extract with the levels identified in the appropriate regulations. Refer to Step 8.0 for quality assurance requirements.

8.0 QUALITY CONTROL

8.1 A minimum of one blank (using the same extraction fluid as used for the samples) for every 20 extractions that have been conducted in an extraction vessel. Refer to Chapter One for additional quality control protocols.

8.2 A matrix spike shall be performed for each waste type (e.g., wastewater treatment sludge, contaminated soil, etc.) unless the result exceeds the regulatory level and the data is being used solely to demonstrate that the waste property exceeds the regulatory level. A minimum of one matrix spike must be analyzed for each analytical batch. As a minimum, follow the matrix spike addition guidance provided in each analytical method.

8.2.1 Matrix spikes are to be added after filtration of the 1312 extract and before preservation. Matrix spikes should not be added prior to 1312 extraction of the sample.

8.2.2 In most cases, matrix spike levels should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration, but may not be less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal volume of 1312 extract as that which was analyzed for the unspiked sample.

8.2.3 The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether

matrix interferences exist. Use of other internal calibration methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the analyte concentration in the 1312 extract when the recovery of the matrix spike is below the expected analytical method performance.

8.2.4 Matrix spike recoveries are calculated by the following formula:

$$\%R \text{ (\% Recovery)} = 100\ (X_s - X_u) / K$$

where:

X_s = measured value for the spiked sample
X_u = measured value for the unspiked sample, and
K = known value of the spike in the sample.

8.3 All quality control measures described in the appropriate analytical methods shall be followed.

8.4 The use of internal calibration quantitation methods shall be employed for a metallic contaminant if: (1) Recovery of the contaminant from the 1312 extract is not at least 50% and the concentration does not exceed the appropriate regulatory level, and (2) The concentration of the contaminant measured in the extract is within 20% of the appropriate regulatory level.

8.4.1. The method of standard additions shall be employed as the internal calibration quantitation method for each metallic contaminant.

8.4.2 The method of standard additions requires preparing calibration standards in the sample matrix rather than reagent water or blank solution. It requires taking four identical aliquots of the solution and adding known amounts of standard to three of these aliquots. The forth aliquot is the unknown. Preferably, the first addition should be prepared so that the resulting concentration is approximately 50% of the expected concentration of the sample. The second and third additions should be prepared so that the concentrations are approximately 100% and 150% of the expected concentration of the sample. All four aliquots are maintained at the same final volume by adding reagent water or a blank solution, and may need dilution adjustment to maintain the signals in the linear range of the instrument technique. All four aliquots are analyzed.

8.4.3 Prepare a plot, or subject data to linear regression, of instrument signals or external-calibration-derived concentrations as the dependant variable (y-axis) versus concentrations of the additions of standards as the independent variable (x-axis). Solve for the intercept of the abscissa (the independent variable, x-axis) which is the concentration in the unknown.

8.4.4 Alternately, subtract the instrumental signal or external-calibration-derived concentration of the unknown (unspiked) sample from the instrumental signals or external-calibration-derived concentrations of the standard additions. Plot or subject to linear regression of the corrected instrument signals or external-calibration-derived concentra-

tions as the dependant variable versus the independent variable. Derive concentrations for the unknowns using the internal calibration curve as if it were an external calibration curve.

8.5 Samples must undergo 1312 extraction within the following time periods:

SAMPLE MAXIMUM HOLDING TIMES (days)

	From: Field Collection To: 1312 extraction	From: 1312 extraction To: Preparative extraction	From: Preparative extraction To: Determinative analysis	Total Elapsed Time
Volatiles	14	NA	14	28
Semi-volatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360
NA = Not Applicable				

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

9.0 METHOD PERFORMANCE

9.1 Precision results for semi-volatiles and metals: An eastern soil with high organic content and a western soil with low organic content were used for the semi-volatile and metal leaching experiments. Both types of soil were analyzed prior to contaminant spiking. The results are shown in Table 6. The concentration of contaminants leached from the soils were reproducible, as shown by the moderate relative standard deviations (RSDs) of the recoveries (averaging 29% for the compounds and elements analyzed).

9.2 Precision results for volatiles: Four different soils were spiked and tested for the extraction of volatiles. Soils One and Two were from western and eastern Superfund sites. Soils Three and Four were mixtures of a western soil with low organic content and two different municipal sludges. The results are shown in Table 7. Extract concentrations of volatile organics from the eastern soil were lower than from the western soil. Replicate leachings of Soils

Three and Four showed lower precision than the leachates from the Superfund soils.

10.0 REFERENCES

1. Environmental Monitoring Systems Laboratory, "Performance Testing of Method 1312; QA Support for RCRA Testing: Project Report". EPA/600/4-89/022. EPA Contract 68-03-3249 to Lockheed Engineering and Sciences Company, June 1989.

2. Research Triangle Institute, "Interlaboratory Comparison of Methods 1310, 1311, and 1312 for Lead in Soil". U.S. EPA Contract 68-01-7075, November 1988.

Table 1. Volatile Analytes[1]

Compound	CAS No.
Acetone	67-64-1
Benzene	71-43-2
n-Butyl alcohol	71-36-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1,-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

[1] When testing for any or all of these analytes, the zero-headspace extractor vessel shall be used instead of the bottle extractor.

Table 2. Suitable Rotary Agitation Apparatus[1]

Company	Location	Model No.
Analytical Testing and Consulting Services, Inc.	Warrington, PA (215) 343-4490	4-vessel extractor (DC20S); 8-vessel extractor (DC20); 12-vessel extractor (DC20B)
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	2-vessel (3740-2); 4-vessel (3740-4); 6-vessel (3740-6); 8-vessel (3740-8); 12-vessel (3740-12); 24-vessel (3740-24)
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	8-vessel (08-00-00) 4-vessel (04-00-00)
IRA Machine Shop and Laboratory	Santurce, PR (809) 752-4004	8-vessel (011001)
Lars Lande Manufacturing	Whitmore Lake, MI (313) 449-4116	10-vessel (10VRE) 5-vessel (5VRE)
Millipore Corp.	Bedford, MA (800) 225-3384	4-ZHE or 4 1-liter bottle extractor (YT300RAHW)

[1] Any device that rotates the extraction vessel in an end-over-end fashion at 30 ±2 rpm is acceptable.

Table 3. Suitable Zero-Headspace Extractor Vessels[1]

Company	Location	Model No.
Analytical Testing & Consulting Services, Inc.	Warrington, PA (215) 343-4490	C102, Mechanical Pressure Device
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	3745-ZHE, Gas Pressure Device
Lars Lande Manufacturing[2]	Whitmore Lake, MI (313) 449-4116	ZHE-11, Gas Pressure Device
Millipore Corporation	Bedford, MA (800) 225-3384	YT30090HW, Gas Pressure Device
Environmental Machine and Design, Inc.	Lynchburg, VA (804) 845-6424	VOLA-TOX1, Gas Pressure Device

[1] Any device that meets the specifications listed in Step 4.2.1 of the method is suitable.

[2] This device uses a 110 mm filter.

Table 4. Suitable Filter Holders[1]

Company	Location	Model/ Catalogue #	Size
Nucleopore Corporation	Pleasanton, CA (800) 882-7711	425910 410400	142 mm 47 mm
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	302400 311400	142 mm 47 mm
Millipore Corporation	Bedford, MA (800) 225-3384	YT30142HW XX1004700	142 mm 47 mm

[1] Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic analytes are of concern. The 142 mm size filter holder is recommended.

Table 5. Suitable Filter Media[1]

Company	Location	Model	Pore Size (μm)
Millipore Corporation	Bedford, MA (800) 225-3384	AP40	0.7
Nucleopore Corporation	Pleasanton, CA (415) 463-2530	211625	0.7
Whatman Laboratory Products, Inc.	Clifton, NJ (201) 773-5800	GFF	0.7
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	GF75	0.7

[1] Any filter that meets the specifications in Step 4.4 of the Method is suitable.

TABLE 6 - METHOD 1312 PRECISION RESULTS FOR SEMI-VOLATILES AND METALS

		Eastern Soil (pH 4.2)		Western Soil (pH 5.0)	
	Amount Spiked (µg)	Amount Recovered* (µg)	% RSD	Amount Recovered* (µg)	% RSD
FORTIFIED ANALYTES					
bis(2-chloroethyl)-ether	1040	834	12.5	616	14.2
2-Chlorophenol	1620	1010	6.8	525	54.9
1,4-Dichlorobenzene	2000	344	12.3	272	34.6
1,2-Dichlorobenzene	8920	1010	8.0	1520	28.4
2-Methylphenol	3940	1860	7.7	1130	32.6
Nitrobenzene	1010	812	10.0	457	21.3
2,4-Dimethylphenol	1460	200	18.4	18	87.6
Hexachlorobutadiene	6300	95	12.9	280	22.8
Acenaphthene	3640	210	8.1	310**	7.7
2,4-Dinitrophenol	1300	896**	6.1	23**	15.7
2,4-Dinitrotoluene	1900	1150	5.4	585	54.4
Hexachlorobenzene	1840	3.7	12.0	10	173.2
gamma BHC (Lindane)	7440	230	16.3	1240	55.2
beta BHC	640	35	13.3	65.3	51.7
METALS					
Lead	5000	70	4.3	10	51.7
Cadmium	1000	387	2.3	91	71.3

* - Triplicate analyses.
** - Duplicate analyses; one value was rejected as an outlier at the 90% confidence level using the Dixon Q test.

TABLE 7 - METHOD 1312 PRECISION RESULTS FOR VOLATILES

Compound Name	Soil No. 1 (Western) Avg. %Rec.*	Soil No. 1 (Western) %RSD	Soil No. 2 (Eastern) Avg. %Rec.*	Soil No. 2 (Eastern) %RSD	Soil No. 3 (Western and Sludge) Avg. %Rec.**	Soil No. 3 (Western and Sludge) %RSD	Soil No. 4 (Western and Sludge) Avg. %Rec.***	Soil No. 4 (Western and Sludge) %RSD
Acetone	44.0	12.4	43.8	2.25	116.0	11.5	21.3	71.4
Acrylonitrile	52.5	68.4	50.5	70.0	49.3	44.9	51.8	4.6
Benzene	47.8	8.29	34.8	16.3	49.8	36.7	33.4	41.1
n-Butyl Alcohol (1-Butanol)	55.5	2.91	49.2	14.6	65.5	37.2	73.0	13.9
Carbon disulfide	21.4	16.4	12.9	49.5	36.5	51.5	21.3	31.5
Carbon tetrachloride	40.6	18.6	22.3	29.1	36.2	41.4	24.0	34.0
Chlorobenzene	64.4	6.76	41.5	13.1	44.2	32.0	33.0	24.9
Chloroform	61.3	8.04	54.8	16.4	61.8	29.1	45.8	38.6
1,2-Dichloroethane	73.4	4.59	68.7	11.3	58.3	33.3	41.2	37.8
1,1-Dichloroethane	31.4	14.5	22.9	39.3	32.0	54.4	16.8	26.4
Ethyl acetate	76.4	9.65	75.4	4.02	23.0	119.8	11.0	115.5
Ethylbenzene	56.2	9.22	23.2	11.5	37.5	36.1	27.2	28.6
Ethyl ether	48.0	16.4	55.1	9.72	37.3	31.2	42.0	17.6
Isobutanol (4-Methyl -1-propanol)	0.0	ND	0.0	ND	61.8	37.7	76.0	12.2
Methylene chloride	47.5	30.3	42.2	42.9	52.0	37.4	37.3	16.6
Methyl ethyl ketone (2-Butanone)	56.7	5.94	61.9	3.94	73.7	31.3	40.6	39.0
Methyl isobutyl ketone	81.1	10.3	88.9	2.99	58.3	32.6	39.8	40.3
1,1,1,2-Tetrachloroethane	69.0	6.73	41.1	11.3	50.8	31.5	36.8	23.8
1,1,2,2-Tetrachloroethane	85.3	7.04	58.9	4.15	64.0	25.7	53.6	15.8
Tetrachloroethene	45.1	12.7	15.2	17.4	26.2	44.0	18.6	24.2
Toluene	59.2	8.06	49.3	10.5	45.7	35.2	31.4	37.2
1,1,1-Trichloroethane	47.2	16.0	33.8	22.8	40.7	40.6	26.2	38.8
1,1,2-Trichloroethane	76.2	5.72	67.3	8.43	61.7	28.0	46.4	25.4
Trichloroethene	54.5	11.1	39.4	19.5	38.8	40.9	25.6	34.1
Trichlorofluoromethane	20.7	24.5	12.6	60.1	28.5	34.0	19.8	33.9
1,1,2-Trichlorotrifluoroethane	18.1	26.7	6.95	58.0	21.5	67.8	15.3	24.8
Vinyl chloride	10.2	20.3	7.17	72.8	25.0	61.0	11.8	25.4

* Triplicate analyses
** Six replicate analyses
*** Five replicate analyses

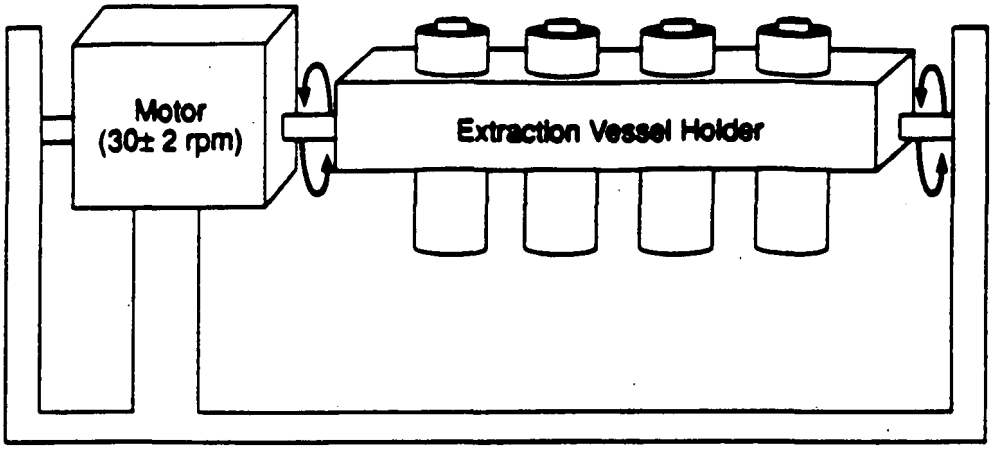


Figure 1. Rotary Agitation Apparatus

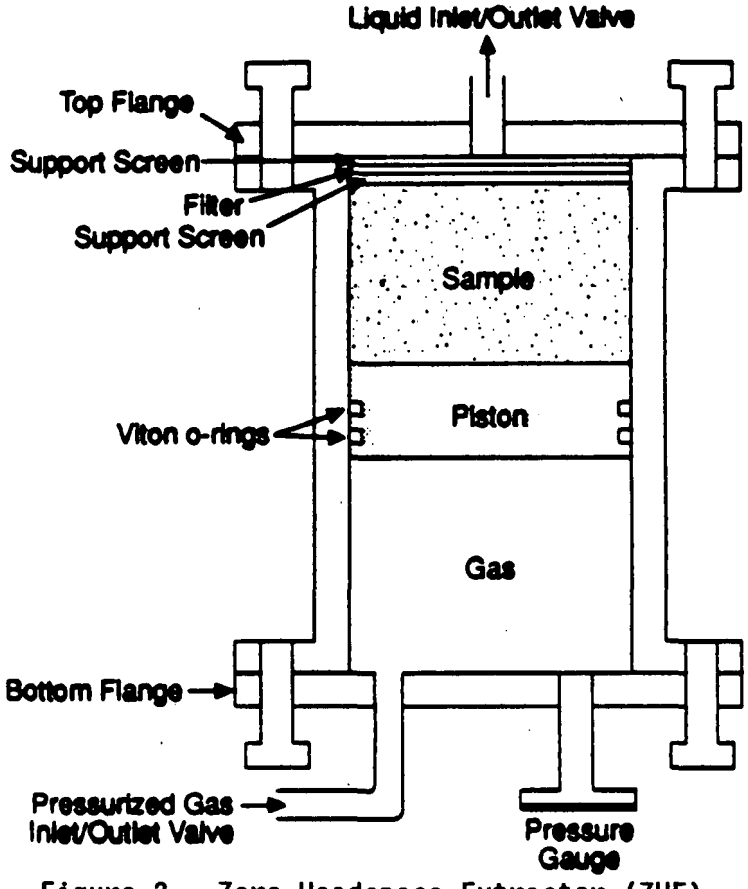
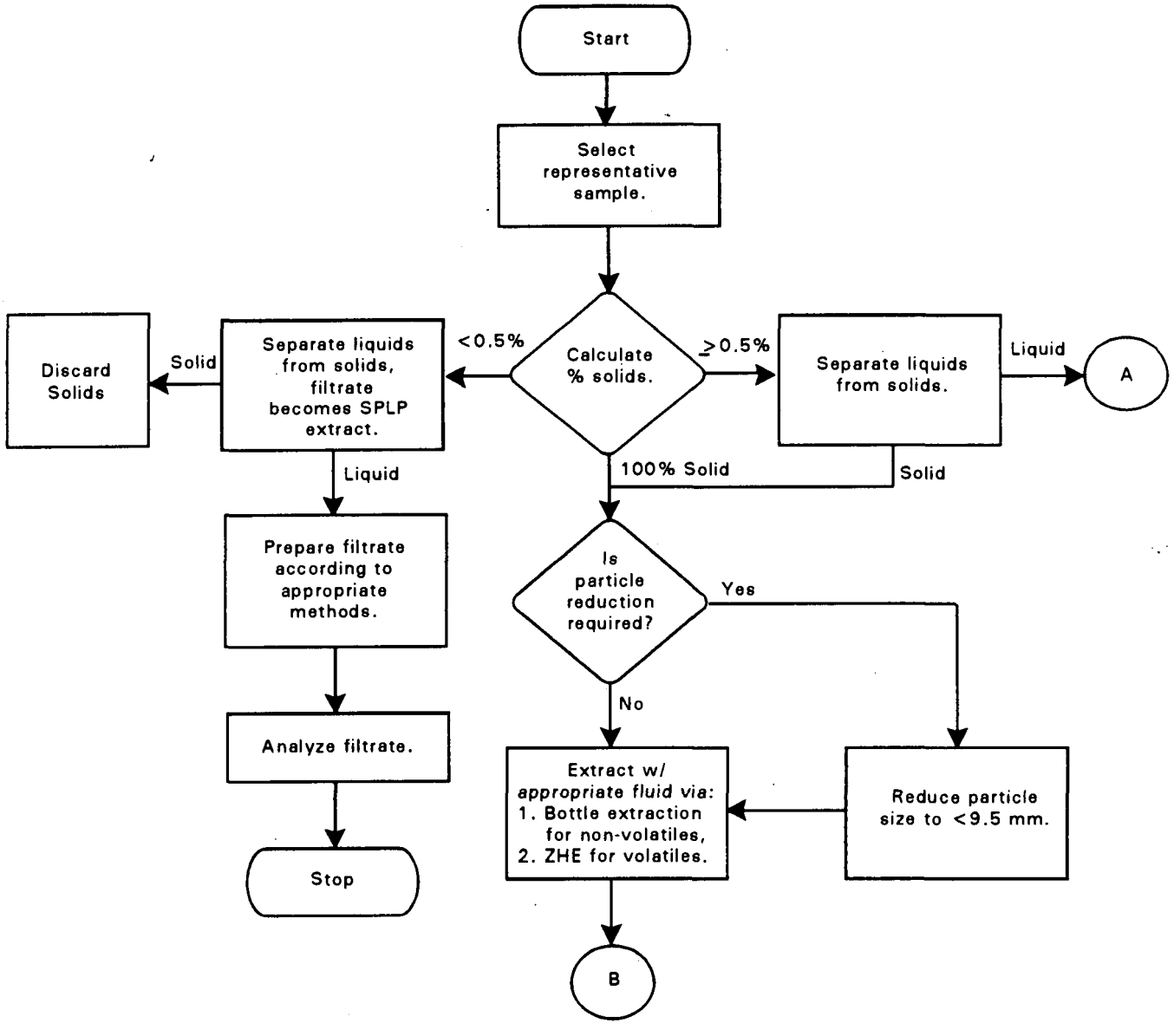


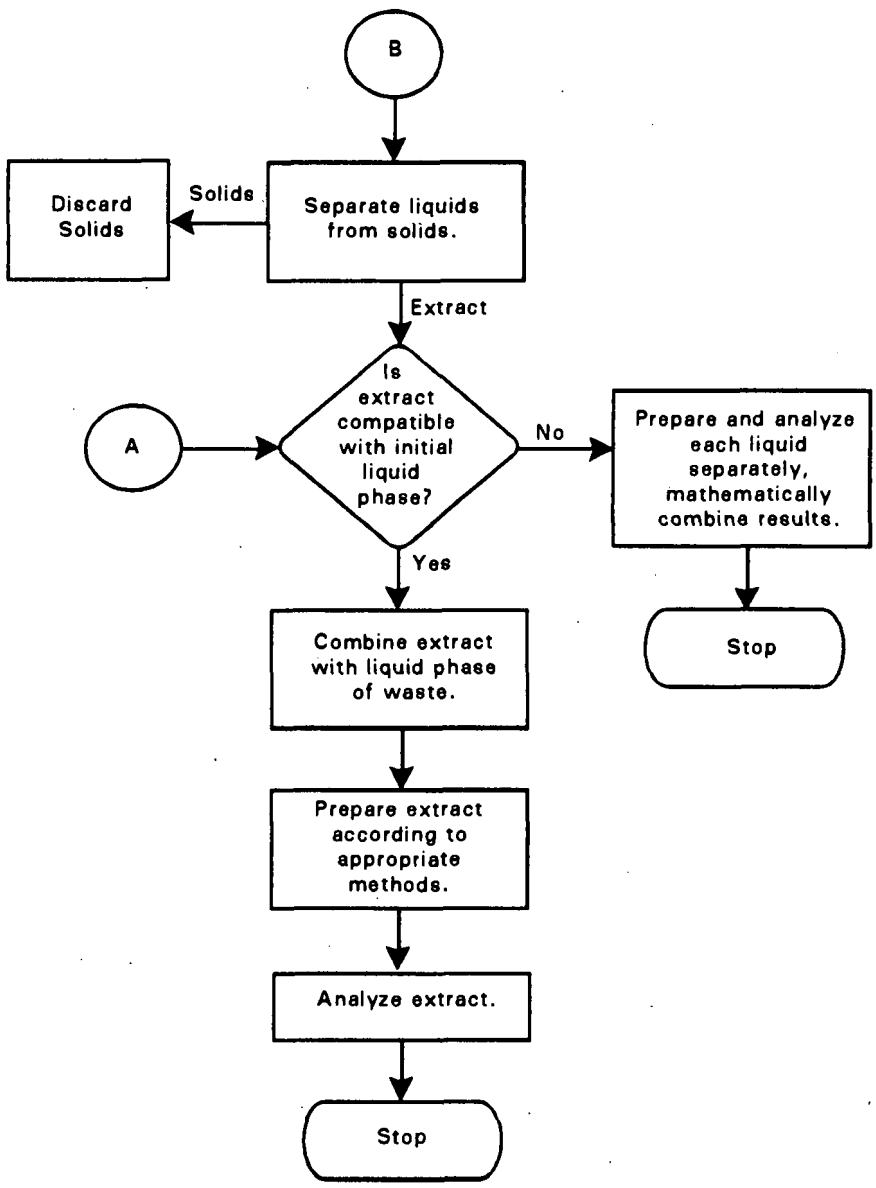
Figure 2. Zero-Headspace Extractor (ZHE)

METHOD 1312

SYNTHETIC PRECIPITATION LEACHING PROCEDURE



SYNTHETIC PRECIPITATION LEACHING PROCEDURE (continued)



METHOD 1330A

EXTRACTION PROCEDURE FOR OILY WASTES

1.0 SCOPE AND APPLICATION

1.1 Method 1330 is used to determine the mobile metal concentration (MMC) in oily wastes.

1.2 Method 1330 is applicable to API separator sludges, rag oils, slop oil emulsions, and other oil wastes derived from petroleum refining.

2.0 SUMMARY OF METHOD

2.1 The sample is separated into solid and liquid components by filtration.

2.2 The solid phase is placed in a Soxhlet extractor, charged with tetrahydrofuran, and extracted. The THF is removed, the extractor is then charged with toluene, and the sample is reextracted.

2.3 The EP method (Method 1310) is run on the dry solid residue.

2.4 The original liquid, combined extracts, and EP leachate are analyzed for the EP metals.

3.0 INTERFERENCES

3.1 Matrix interferences will be coextracted from the sample. The extent of these interferences will vary considerably from waste to waste, depending on the nature and diversity of the particular refinery waste being analyzed.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extraction apparatus.

4.2 Vacuum pump or other source of vacuum.

4.3 Buchner funnel 12.

4.4 Electric heating mantle.

4.5 Paper extraction thimble.

4.6 Filter paper.

4.7 Muslin cloth disks.

4.8 Evaporative flask - 250-mL.

4.9 Balance - Analytical, capable of weighing to ± 0.5 mg.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Tetrahydrofuran, C_4H_8O.

5.4 Toluene, $C_6H_5CH_3$.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Samples must be collected in glass containers having a total volume of at least 150 mL. No solid material should interfere with sealing the sample container.

6.2 Sampling devices should be wiped clean with paper towels or absorbent cloth, rinsed with a small amount of hexane followed by acetone rinse, and dried between samples. Alternatively, samples can be taken with disposable sampling devices in beakers.

7.0 PROCEDURE

7.1 Separate the sample (minimum 100 g) into its solid and liquid components. The liquid component is defined as that portion of the sample which passes through a 0.45 μm filter media under a pressure differential of 75 psi.

7.2 Determine the quantity of liquid (mL) and the concentration of the toxicants of concern in the liquid phase (mg/L).

7.3 Place the solid phase into a Soxhlet extractor, charge the concentration flask with 300 mL tetrahydrofuran, and extract for 3 hours.

7.4 Remove the flask containing tetrahydrofuran and replace it with one containing 300 mL toluene.

7.5 Extract the solid a second time, for 3 hours, with the toluene.

7.6 Combine the tetrahydrofuran and toluene extracts.

7.7 Analyze the combined extracts for the toxicants of concern.

7.8 Determine the quantity of liquid (mL) and the concentration of the toxicants of concern in the combined extracts (mg/L).

7.9 Take the solid material remaining in the Soxhlet thimble and dry it at 100°C for 30 minutes.

7.10 Run the EP (Method 1310) on the dried solid.

7.11 Calculate the mobile metal concentration (MMC) in mg/L using the following formula:

$$MMC = 1{,}000 \times \frac{(Q_1 + Q_2 + Q_3)}{(L_1 + L_2 + L_3)}$$

where:

Q_1 = Mass of toxicant in initial liquid phase of sample (amount of liquid x concentration of toxicant) (mg).

Q_2 = Mass of toxicant in combined organic extracts of sample (amount of liquid x concentration of toxicant) (mg).

Q_3 = Mass of toxicant in EP extract of solid (amount of extract x concentration of toxicant) (mg).

L_1 = Volume of initial liquid (mL).

L_2 = Volume of liquid in THF and toluene extract (Step 7.8) (mL).

L_3 = Volume of liquid in EP (mL) = 20 x [weight of dried solid from Step 7.9 (g)].

8.0 QUALITY CONTROL

8.1 Any reagent blanks or replicates samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

Figure 1. Extractor

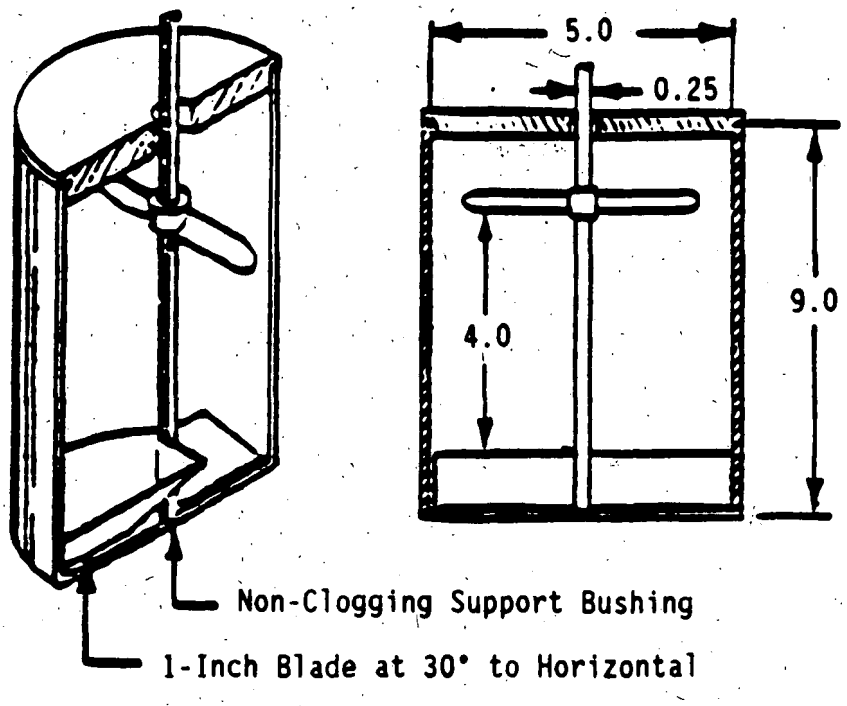


Figure 2. Rotary Extractor

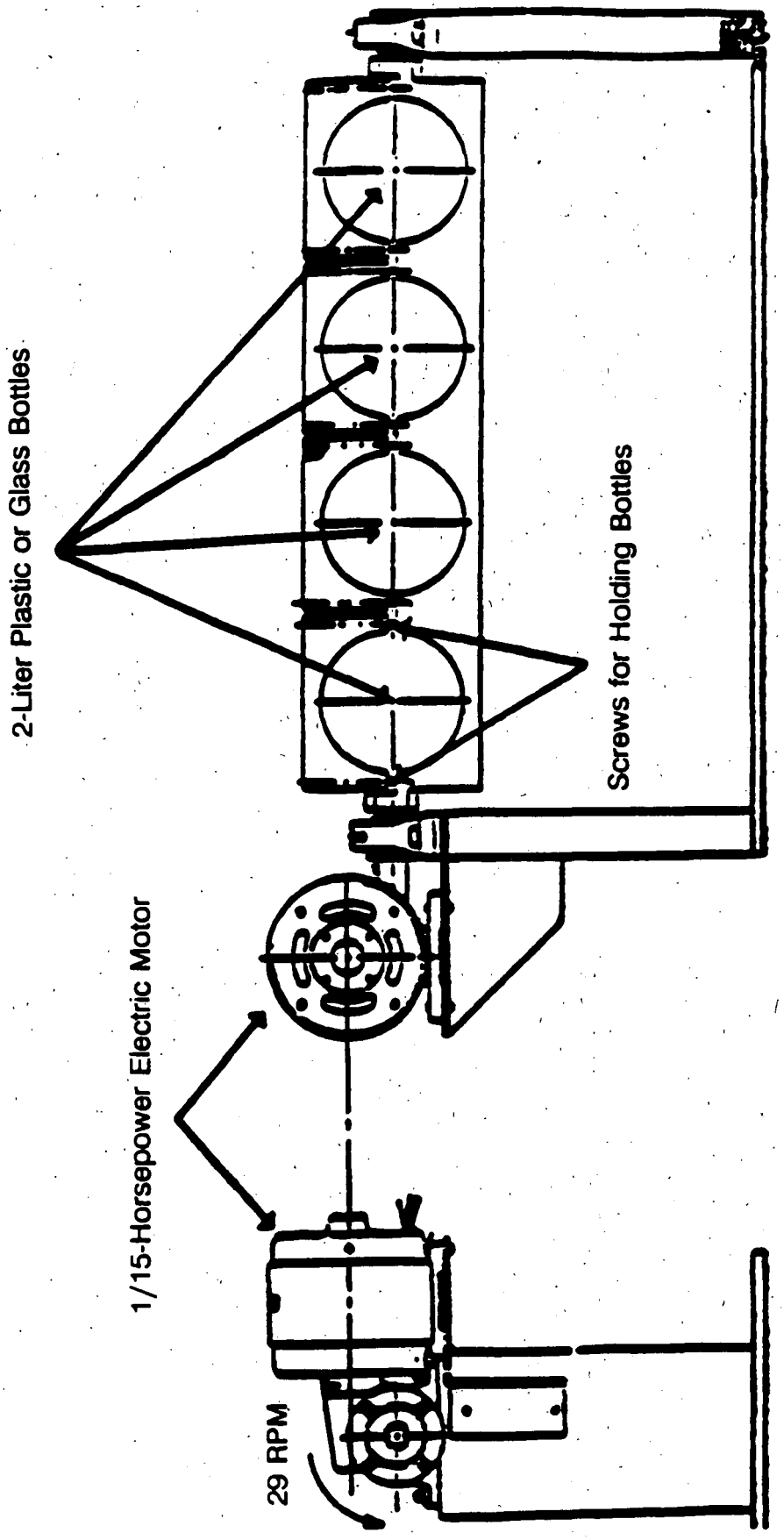


Figure 3. EPRI Extractor

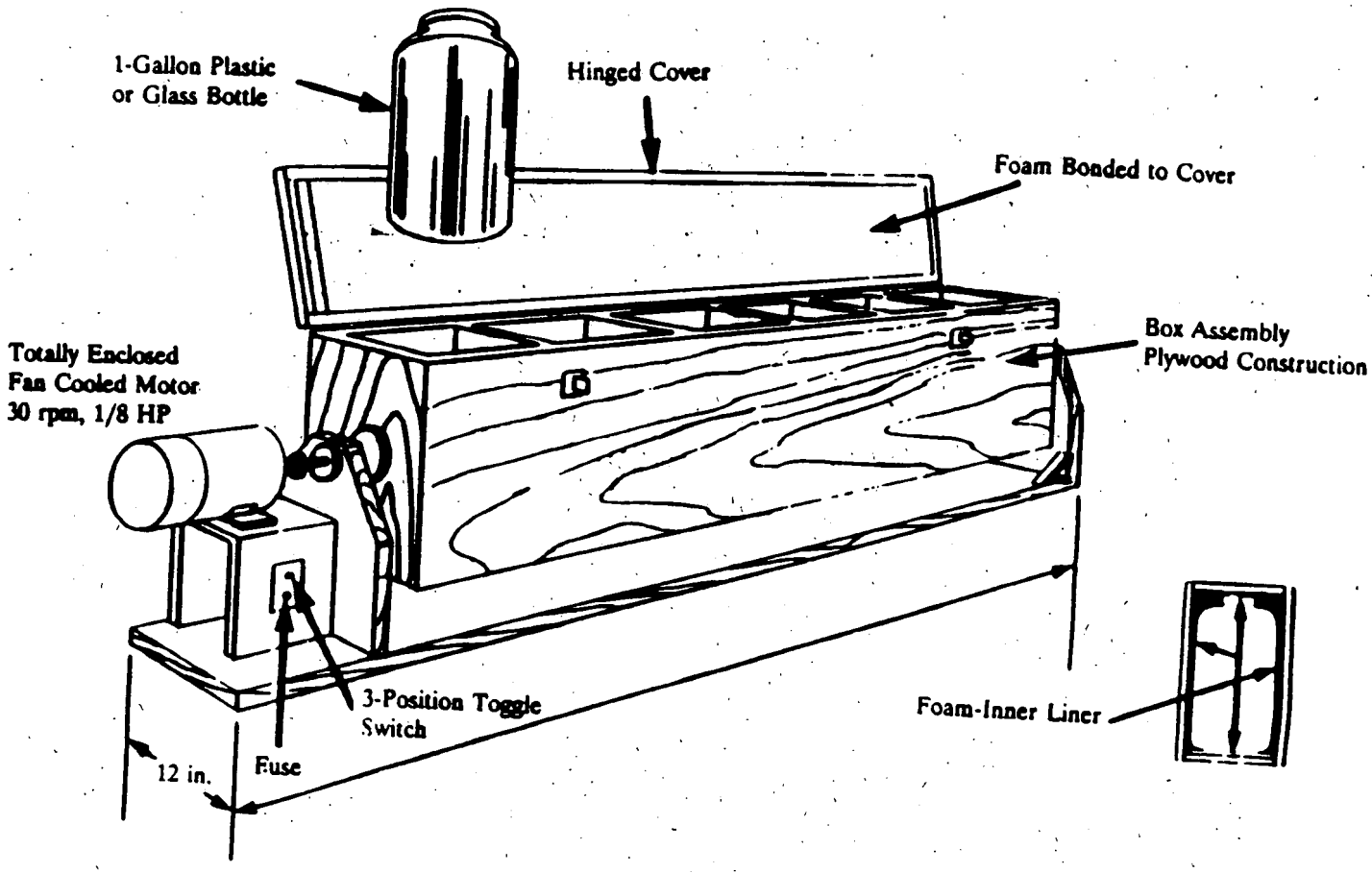
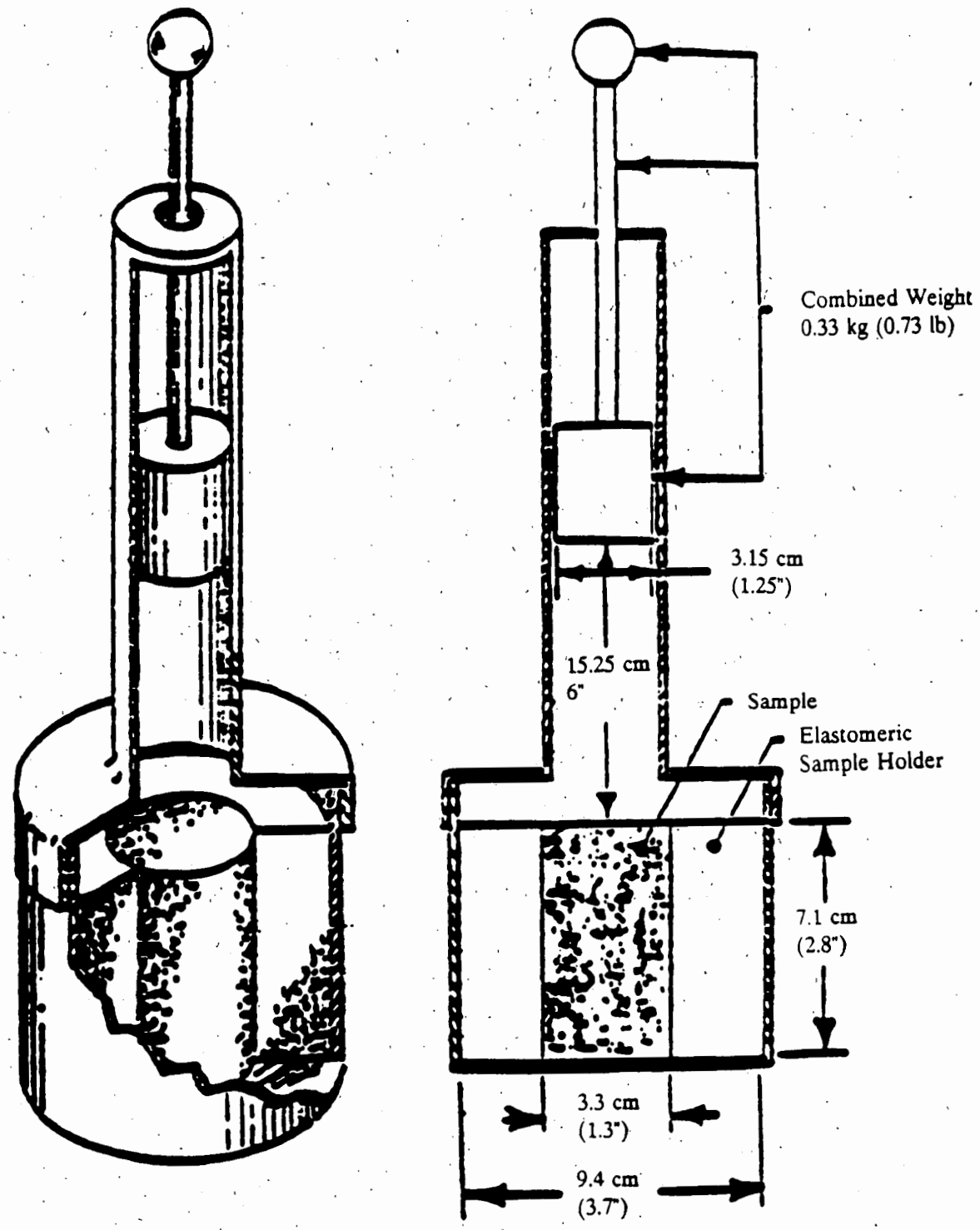
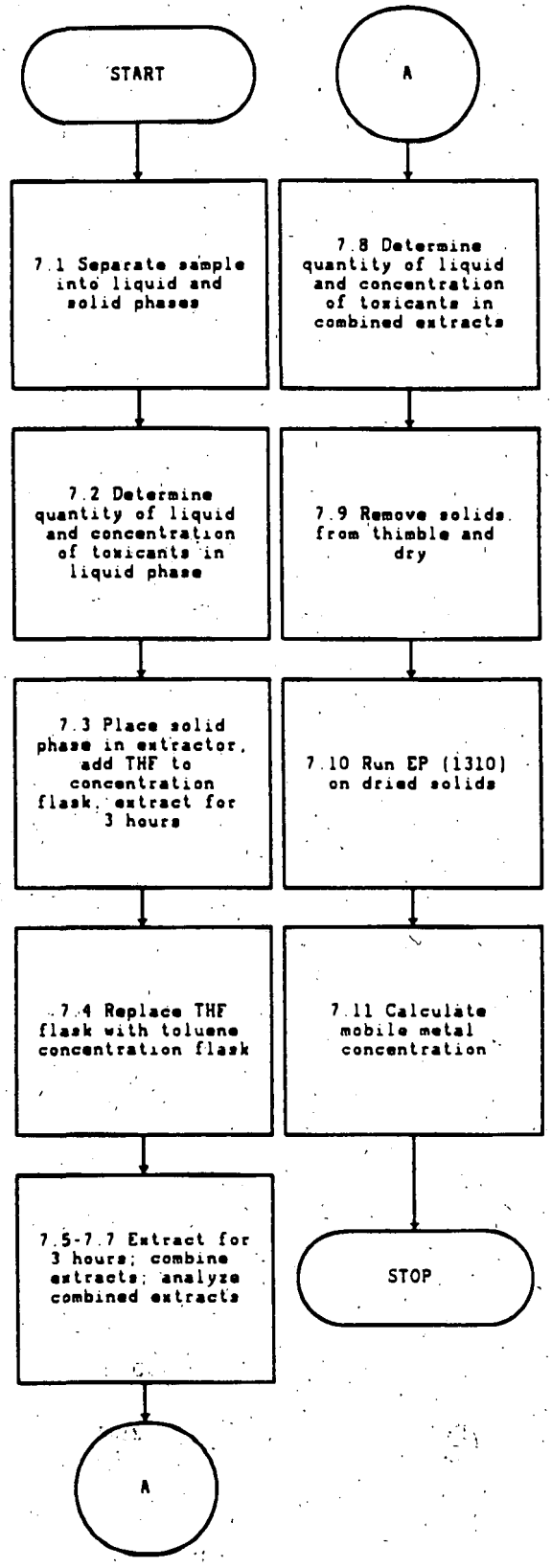


Figure 4. Compaction Tester



METHOD 1330A
EXTRACTION PROCEDURE FOR OILY WASTE



METHOD 3005A

ACID DIGESTION OF WATERS FOR TOTAL RECOVERABLE OR DISSOLVED METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 Method 3005 is an acid digestion procedure used to prepare surface and ground water samples for analysis by flame atomic absorption spectroscopy (FLAA) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by Method 3005 may be analyzed by AAS or ICP for the following metals:

Aluminum	Magnesium
Antimony**	Manganese
Arsenic*	Molybdenum
Barium	Nickel
Beryllium	Potassium
Cadmium	Selenium*
Calcium	Silver
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

* ICP only
**May be analyzed by ICP, FLAA, or GFAA

1.2 When analyzing for total dissolved metals filter the sample, at the time of collection, prior to acidification with nitric acid.

2.0 SUMMARY OF METHOD

2.1 Total recoverable metals - The entire sample is acidified at the time of collection with nitric acid. At the time of analysis the sample is heated with acid and substantially reduced in volume. The digestate is filtered and diluted to volume, and is then ready for analysis.

2.2 Dissolved metals - The sample is filtered through a 0.45-μm filter at the time of collection and the liquid phase is then acidified at the time of collection with nitric acid. Samples for dissolved metals do not need to be digested as long as the acid concentrations have been adjusted to the same concentration as in the standards.

3.0 INTERFERENCES

3.1 The analyst should be cautioned that this digestion procedure may not be sufficiently vigorous to destroy some metal complexes.

Precipitation will cause a lowering of the silver concentration and therefore an inaccurate analysis.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers of assorted sizes or equivalent.

4.2 Watch glasses or equivalent.

4.3 Qualitative filter paper and filter funnels.

4.4 Graduated cylinder or equivalent.

4.5 Electric hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95°C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine level of impurities. If method blank is < MDL, then acid can be used.

5.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If method blank is < MDL, then acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Both plastic and glass containers are suitable.

6.3 Sampling

6.3.1 Total recoverable metals - All samples must be acidified at the time of collection with HNO_3 (5 mL/L).

6.3.2 Dissolved metals - All samples must be filtered through a 0.45-μm filter and then acidified at the time of collection with HNO_3 (5 mL/L).

7.0 PROCEDURE

7.1 Transfer a 100-mL aliquot of well-mixed sample to a beaker.

7.2 For metals that are to be analyzed, add 2 mL of concentrated HNO_3 and 5 mL of concentrated HCl. The sample is covered with a ribbed watch glass or other suitable covers and heated on a steam bath, hot plate or other heating source at 90 to 95°C until the volume has been reduced to 15-20 mL.

CAUTION: Do not boil. Antimony is easily lost by volatilization from hydrochloric acid media.

7.3 Remove the beaker and allow to cool. Wash down the beaker walls and watch glass with water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer; this additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO_3.

7.4 Adjust the final volume to 100 mL with reagent water.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, blanks should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. Replicate samples will be used to determine precision. The sample load will dictate the frequency, but 5% is recommended. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each batch. Refer to Chapter One for the proper protocol when analyzing spikes.

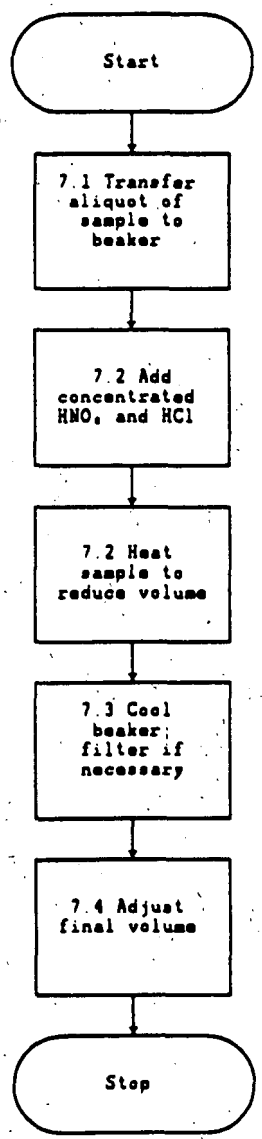
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.


Start
7.1 Transfer aliquot of sample to beaker
7.2 Add concentrated HNO_3 and HCl
7.2 Heat sample to reduce volume
7.3 Cool beaker; filter if necessary
7.4 Adjust final volume
Stop

3010A

METHOD 3010A

ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS FOR TOTAL METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for analysis, by flame atomic absorption spectroscopy (FLAA) or inductively coupled argon plasma spectroscopy (ICP). The procedure is used to determine total metals.

1.2 Samples prepared by Method 3010 may be analyzed by FLAA or ICP for the following:

Aluminum	Magnesium
*Arsenic	Manganese
Barium	Molybdenum
Beryllium	Nickel
Cadmium	Potassium
Calcium	*Selenium
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

* Analysis by ICP

NOTE: See Method 7760 for the digestion and FLAA analysis of Silver.

1.3 This digestion procedure is not suitable for samples which will be analyzed by graphite furnace atomic absorption spectroscopy because hydrochloric acid can cause interferences during furnace atomization. Consult Method 3020A for samples requiring graphite furnace analysis.

2.0 SUMMARY OF METHOD

2.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is refluxed with hydrochloric acid and brought up to volume. If sample should go to dryness, it must be discarded and the sample reprepared.

3.0 INTERFERENCES

3.1 Interferences are discussed in the referring analytical method.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers - 150-mL or equivalent.

4.2 Watch glasses - Ribbed and plain or equivalent.

4.3 Qualitative filter paper or centrifugation equipment.

4.4 Graduated cylinder or equivalent - 100mL.

4.5 Funnel or equivalent.

4.6 Hot plate or equivalent heating source - adjustable and capable of maintaining a temperature of 90-95°C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine levels of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrochloric acid (1:1), HCl. Prepared from water and hydrochloric acid. Hydrochloric acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3, for further information.

6.3 Aqueous wastewaters must be acidified to a pH of < 2 with HNO_3.

7.0 PROCEDURE

7.1 Transfer a 100-mL representative aliquot of the well-mixed sample to a 150-mL Griffin beaker and add 3 mL of concentrated HNO_3. Cover the beaker with a ribbed watch glass or equivalent. Place the beaker on a hot plate or

equivalent heating source and cautiously evaporate to a low volume (5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3-mL portion of concentrated HNO_3. Cover the beaker with a nonribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

NOTE: If a sample is allowed to go to dryness, low recoveries will result. Should this occur, discard the sample and reprepare.

7.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, uncover the beaker or use a ribbed watch glass, and evaporate to a low volume (3 mL), not allowing any portion of the bottom of the beaker to go dry. Cool the beaker. Add a small quantity of 1:1 HCl (10 mL/100 mL of final solution), cover the beaker, and reflux for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

7.3 Wash down the beaker walls and watch glass with water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned. Rinse the filter and filter apparatus with dilute nitric acid and discard the rinsate. Filter the sample and adjust the final volume to 100 mL with reagent water and the final acid concentration to 10%. The sample is now ready for analysis.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, blanks should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. A replicate sample should be processed with each analytical batch or every 20 samples, whichever is greater. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each batch of samples processed and whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spikes.

8.5 The method of standard addition shall be used for the analysis of all EP extracts and delisting petitions (see Method 7000, Step 8.7). Although not required, use of the method of standard addition is recommended for any sample

that is suspected of having an interference.

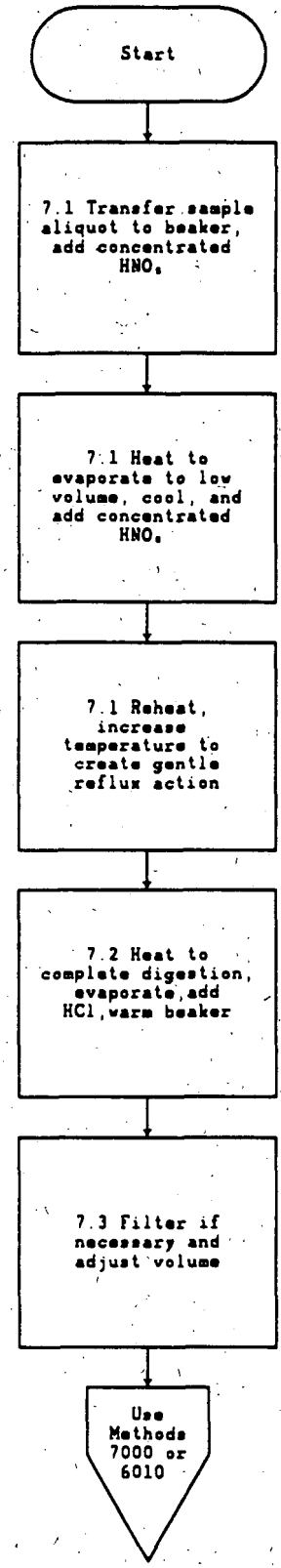
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.


Start
7.1 Transfer sample aliquot to beaker, add concentrated HNO_3
7.1 Heat to evaporate to low volume, cool, and add concentrated HNO_3
7.1 Reheat, increase temperature to create gentle reflux action
7.2 Heat to complete digestion, evaporate, add HCl, warm beaker
7.3 Filter if necessary and adjust volume
Use Methods 7000 or 6010

METHOD 3015

MICROWAVE ASSISTED ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for analysis, by flame atomic absorption spectroscopy (FLAA), graphite furnace absorption spectroscopy (GFAA), inductively coupled argon plasma spectroscopy (ICP), or inductively coupled argon plasma mass spectrometry (ICP-MS). The procedure is a hot acid leach for determining available metals. Due to the rapid advances in microwave technology, consult your manufacturer's recommended instructions for guidance on their microwave digestion system and refer to the SW-846 "DISCLAIMER" when conducting analyses using Method 3015.

1.2 Samples prepared by Method 3015 using nitric acid digestion may be analyzed by FLAA, GFAA, ICP-AES, or ICP-MS for the following:

Aluminum	Lead
Antimony	Magnesium
Arsenic*	Manganese
Barium	Molybdenum
Beryllium	Nickel
Cadmium	Potassium
Calcium	Selenium*
Chromium	Silver
Cobalt	Sodium
Copper	Thallium
Iron	Vanadium
	Zinc

*Cannot be analyzed by FLAA

2.0 SUMMARY OF METHOD

2.1 A representative 45 mL aqueous sample is digested in 5 mL of concentrated nitric acid in a fluorocarbon (PFA or TFM) digestion vessel for 20 minutes using microwave heating. After the digestion process, the sample is cooled, and then filtered, centrifuged, or allowed to settle in a clean sample bottle prior to analysis.

3.0 INTERFERENCES

3.1 Many samples that contain organics, such as TCLP extracts, will result in higher vessel pressures which have the potential to cause venting of the vessels. Venting can result in either loss of analytes and/or sample, which must be avoided. A smaller sample size can be used but the final water volume

prior to nitric acid addition must remain at 45 mL. This is required to retain the heat characteristics of the calibration procedure. Limits of quantitation will change with sample quantity (dilution) as with instrumentation."

4.0 APPARATUS AND MATERIALS

4.1 Microwave apparatus requirements

4.1.1 The microwave unit provides programmable power with a minimum of 574 W, which can be programmed to within ± 10 W of the required power. Typical units provide a nominal 600 W to 1200 W of power. Temperature monitoring and control of the microwave unit are desirable.

4.1.2 The microwave unit cavity is corrosion resistant and well ventilated.

4.1.3 All electronics are protected against corrosion for safe operation.

4.1.4 The system requires fluorocarbon (PFA or TFM) digestion vessels (120 mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psig) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psig).

4.1.5 A rotating turntable is employed to insure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.

> CAUTION: Those laboratories now using or contemplating the use of kitchen type microwave ovens for this method should be aware of several significant safety issues. First, when an acid such as nitric is used to assist sample digestion in microwave units in open vessels, or sealed vessels equipped with venting features, there is the potential for the acid gases released to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened. This can result in operator exposure to microwave energy. Use of a unit with corrosion resistant safety devices prevents this from occurring.

> CAUTION: The second safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures but must be safely contained. However, many digestion vessels constructed from certain fluorocarbons may crack, burst, or explode in the oven under certain pressures. Only unlined fluorocarbon (PFA or TFM) containers with pressure relief mechanisms or containers with fluorocarbon (PFA or TFM) liners and pressure relief mechanisms are considered acceptable at present.

Users are therefore advised not to use kitchen type microwave ovens or to use sealed containers without pressure relief valves for microwave acid digestions by this method. Use of laboratory grade microwave equipment is required to prevent safety hazards. For further information consult reference 1.

CAUTION: In addition, there are many safety and operational recommendations specific to the model and manufacturer of the microwave equipment used in individual laboratories. These specific suggestions are beyond the scope of this method and require the analyst to consult the specific equipment manual, manufacturer and literature for proper and safe operation of the microwave equipment and vessels.

4.2 Volumetric graduated cylinder, 50 or 100 mL capacity or equivalent.

4.3 Filter paper, qualitative or equivalent.

4.4 Analytical balance, 300 g capacity, minimum accuracy ± 0.01 g.

4.5 Filter funnel, glass or disposable polypropylene.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified (Ref. 2).

5.3 Concentrated nitric acid, HNO_3. Acid should be analyzed to determine levels of impurities. If the method blank is less than the MDL, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic containers are preferable. See Chapter Three, Step 3.1.3 of this manual, for further information.

6.3 Aqueous waste waters must be acidified to a pH of < 2 with HNO_3.

7.0 PROCEDURE

7.1 Calibration of Microwave Equipment

NOTE: If the microwave unit uses temperature feedback control capable of replicating the performance specifications of the method, then the calibration procedure may be omitted.

7.1.1 Measurement of the available power for heating is evaluated so that absolute power in watts may be transferred from one microwave unit to another. For cavity type microwave equipment, this is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the unit. The calibration format required for laboratory microwave units depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few units have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a three-point calibration method (7.1.3), otherwise, the analyst must use the multiple point calibration method (7.1.2).

7.1.2 The multiple point calibration involves the measurement of absorbed power over a large range of power settings. Typically, for a 600 W unit, the following power settings are measured; 100,99,98,97, 95,90,80,70,60,50, and 40% using the procedure described in section 7.1.4. This data is clustered about the customary working power ranges. Nonlinearity has been commonly encountered at the upper end of the calibration. If the unit's electronics are known to have nonlinear deviations in any region of proportional power control, it will be necessary to make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. This setting should be checked periodically to evaluate the integrity of the calibration. If a significant change is detected (±10 W), then the entire calibration should be reevaluated.

7.1.3 The three-point calibration involves the measurement of absorbed power at three different power settings. Measure the power at 100% and 50% using the procedure described in section 7.1.4, and calculate the power setting corresponding to the required power in watts specified in the procedure from the (2-point) line. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power within ±10 W, use the multiple point calibration in 7.1.2. This point should also be used to periodically verify the integrity of the calibration.

7.1.4 Equilibrate a large volume of water to room temperature (23 ± 2 °C). One kg of reagent water is weighed (1,000.0 g ± 0.1 g) into a fluorocarbon (PFA or TFM) beaker or a beaker made of some other material that does not significantly absorb microwave energy (glass

absorbs microwave energy and is not recommended). The initial temperature of the water should be 23 ± 2 °C measured to ± 0.05 °C. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the unit's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation and record the maximum temperature within the first 30 seconds to ± 0.05 °C. Use a new sample for each additional measurement. If the water is reused both the water and the beaker must have returned to 23 ± 2 °C. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship

$$P = \frac{(K)\ (C_p)\ (m)\ (\Delta T)}{t} \qquad \text{Eq. 1}$$

Where:

P = the apparent power absorbed by the sample in watts (W). (W=joule·sec^{-1})

K = the conversion factor for thermochemical calories·sec^{-1} to watts (=4.184)

C_p = the heat capacity, thermal capacity, or specific heat (cal·g^{-1}·°C^{-1}), of water

m = the mass of the water sample in grams (g)

ΔT = the final temperature minus the initial temperature (°C)

t = the time in seconds (s)

Using the experimental conditions of 2 minutes and 1 kg of distilled water (heat capacity at 25 °C is 0.9997 cal·g^{-1}·°C^{-1}) the calibration equation simplifies to:

$$P = (\Delta T)\ (34.86)$$

<u>NOTE</u>: Stable line voltage is necessary for accurate and reproducible calibration and operation. The line voltage should be within manufacturer's specification, and during measurement and operation not vary by more than ±2 V. A constant power supply may be necessary for microwave use if the source of the line voltage is unstable.

Electronic components in most microwave units are matched to the units' function and output. When any part of the high voltage circuit, power source, or control components in the unit have been serviced or replaced, it will be necessary to recheck the units' calibration power. If the power output has changed significantly (±10 W), then the entire calibration should be reevaluated.

7.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between high solids (concentrated) samples and low solids (low concentration) samples all digestion vessels should be cleaned by leaching with hot (1:1) hydrochloric acid (greater than 80°C, but less than boiling) for a minimum of two hours followed with hot (1:1) nitric acid (greater than 80°C, but less than boiling) for a minimum of two hours, rinsed with reagent water, and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric or glass volumetric ware and storage containers should be cleaned by leaching with more dilute acids (approximately 10% V/V) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment. In addition, to avoid precipitation of silver, ensure that all HCl has been rinsed from the vessels.

7.3 Sample Digestion

7.3.1 Weigh the fluorocarbon (PFA or TFM) digestion vessel, valve and cap assembly to 0.01 g prior to use.

7.3.2 A 45 mL aliquot of a well shaken sample is measured in a graduated cylinder. This aliquot is poured into the digestion vessel with the number of the vessel recorded on the preparation sheet.

7.3.3 A blank sample of reagent water is treated in the same manner along with spikes and duplicates.

7.3.4 Add 5 mL of concentrated nitric acid to each vessel that will be used. Check to make sure the pressure relief disks are in the caps with the smooth side toward the sample and start the caps a few turns on the vessels. Finish tightening the caps in the capping station which will tighten them to a uniform torque pressure of 12 ft-lbs. (16 N-m) or to the manufacturers recommended specifications. Weigh each capped vessel to the nearest 0.01 g.

> CAUTION: Toxic nitrogen oxide fumes may be evolved, therefore all work must be performed in a properly operating ventilation system. The analyst should also be aware of the potential for a vigorous reaction. If a vigorous reaction occurs, allow to cool before capping the vessel.

7.3.5 Evenly distributed the vessels in the carousel according to the manufacturer's recommended specifications. Blanks are treated as samples for the purpose of balancing the power input. When fewer

than the recommended number of samples are digested, the remaining vessels should be filled with 45 mL of reagent water and 5 mL of nitric acid to achieve the full compliment of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity (Ref. 1).

7.3.6 Program the microwave unit according to the manufacturer's recommended specifications and, if used, connect the pressure vessels to the central overflow vessel with PFA-fluorocarbon tubes. The chosen sequence will bring the samples to 160°C ± 4°C in 10 minutes and will permit a slow rise to 165-170 °C during the second 10 minutes (Ref. 3). Start the turntable motor and be sure the vent fan is running on high and the turntable is turning. Start the microwave generator.

7.3.6.1 Newer microwave units are capable of higher power that permit digestion of a larger number of samples per batch. If the analyst wishes to digest more samples at a time, the analyst may use different power settings as long as they result in the same time and temperature conditions defined in 7.3.6. That is, any sequence of power that brings the samples to 160°C ± 4°C in 10 minutes and permits a slow rise to 165-170°C during the second 10 minutes (Ref. 2).

Issues of safety, structural integrity (both temperature and pressure limitations), heat loss, chemical compatibility, microwave absorption of vessel material, and energy transport will be considerations made in choosing alternative vessels. If all of the considerations are met and the appropriate power settings are provided to reproduce the reaction conditions defined in 7.3.6, then these alternative vessels may be used (Ref. 1,3)

7.3.7 At the end of the microwave program, allow the vessels to cool for at least 5 minutes in the unit before removal to avoid possible injury if a vessel vents immediately after microwave heating. The samples may be cooled outside the unit by removing the carousel and allowing the samples to cool on the bench or in a water bath. When the vessels have cooled to room temperature, weigh and record the weight of each vessel assembly. If the weight of the sample plus acid has decreased by more than 10% discard the sample.

7.3.8 Complete the preparation of the sample by carefully uncapping and venting each vessel in a fume hood. Transfer the sample to an acid-cleaned bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, the sample may be centrifuged, allowed to settle or filtered.

7.3.8.1 Centrifugation: Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.3.8.2 Settling: Allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

7.3.8.3 Filtering: The filtering apparatus must be thoroughly cleaned and prerinsed with dilute (approximately 10% V/V) nitric acid. Filter the sample through qualitative filter paper into a second acid-cleaned container.

7.3.9 The concentration values obtained from analysis must be corrected for the dilution factor from the acid addition. If the sample will be analyzed by ICP-MS additional dilution will generally be necessary. For example, the sample may be diluted by a factor of 20 with reagent water and the acid strength adjusted back to 10% prior to analysis. The dilutions used should be recorded and the measured concentrations adjusted accordingly (e.g., for a 45 mL sample and 5 mL of acid the correction factor is 1.11).

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One, of this Manual, should be followed.

8.2 For each analytical batch of samples processed, analytical reagent blanks (also field blanks if they were taken) should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.3 Duplicate samples should be processed on a routine basis. A duplicate sample is a real sample brought through the whole sample preparation and analytical process. A duplicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Refer to Table 1 for a summary of performance data.

10.0 REFERENCES

1. Introduction to Microwave Sample Preparation: Theory and Practice, Kingston, H. M.; Jassie, L. B., Eds.; ACS Professional Reference Book Series: American Chemical Society, Washington, DC, 1988; Ch 6 & 11.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

3. Kingston, H. M., Final Report EPA IAG #DWI3932541-01-I, September 30, 1988, Appendix A.

4. Shannon, M., Alternate Test Procedure Application, USEPA Region V, Central Regional Laboratory, 536 S. Clark Street, Chicago, IL 60606, 1989.

5. Kingston, H. M., Walter, P. J., "Comparison of Microwave Versus Conventional Dissolution for Environmental Applications", Spectroscopy, vol. 7 No. 9,20-27,1992.

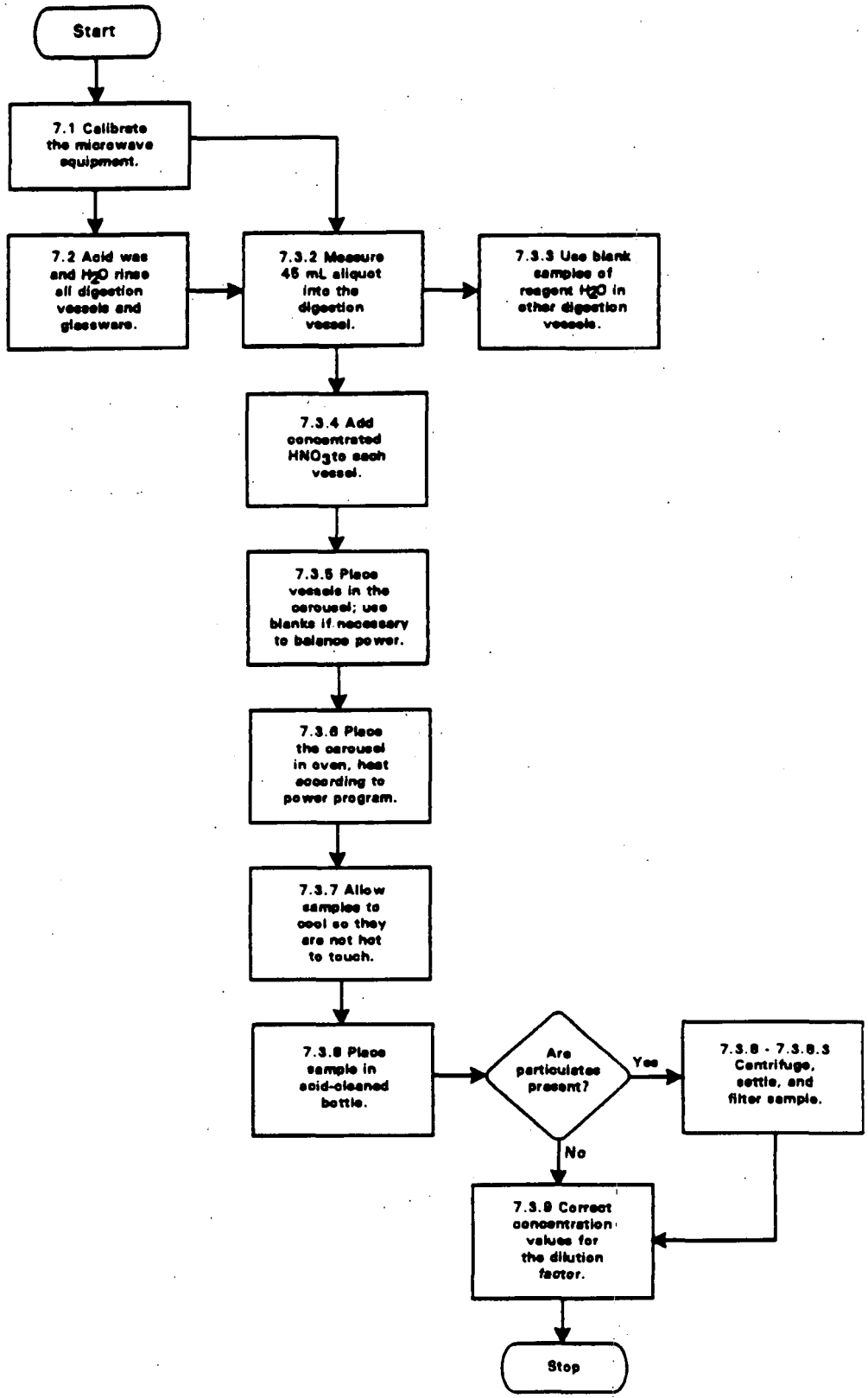
6. Sosinski, P., and Sze C., "Absolute Accuracy Study, Microwave Digestion Method 3015 (Nitric acid only)"; EPA Region III Central Regional Laboratory, 1991.

TABLE 1
MICROWAVE DIGESTION METHOD 3015 (Nitric Acid Only)

Elem	Material	Certified Mean	Observed Mean	Std. Dev.	Relative Standard Deviation	Relative Bias
Al	Tm-11	510.0	485.5	26.3	5.4	-4.80%
Al	Tm-12	2687.0	2770.6	88.2	3.2	3.11%
Al	T-107	220.0	213.5	19.3	9.0	-2.95%
Al	T-109	113.0	117.7	30.6	2.6	4.16%
Ba	Tm-11	450.0	441.4	23.4	5.3	-1.90%
Ba	Tm-12	2529.0	2431.4	70.3	2.9	-3.86%
Ba	T-107	192.0	196.6	15.9	8.1	2.44%
Cd	Tm-11	40.8	44.6	2.1	4.7	9.46%
Cd	Tm-12	237.0	242.3	8	3.3	2.25%
Cd	T-107	14.3	12.4	0.9	7.2	-12.94%
Cd	T-109	12.1	10.3	1.7	16.5	-14.55%
Zn	Tm-11	55.4	55.9	2.6	4.6	1.06%
Zn	Tm-12	314.0	316.5	8.9	2.8	0.82%
Zn	T-107	75.8	81.6	3.3	4.0	7.68%
Zn	T-109	74.0	69.9	4.1	5.8	-5.46%
As	T-107	10.8	12.8	0.84	6.5	19.26%
As	T-109	8.15	90.6	11.0	12.2	11.26%
Co	Tm-11	227.0	242.6	14.1	5.8	6.90%
Co	Tm-12	1067.0	1153.3	35.9	3.1	8.09%
K	T-95	4700.0	5080.3	784	15.4	8.09%
K	T-109	2330.0	2601.5	383.4	14.7	11.65%
Ni	Tm-11	264.0	284.3	16.5	5.8	7.71%
Ni	Tm-12	1234.0	1293.0	39.4	3.0	4.79%
Ni	T-109	57.0	60.8	3.09	5.0	6.72%
Pb	Tm-11	275.0	275.9	32.2	11.7	0.36%
Pb	Tm-12	1326.0	1359.0	35.0	2.6	2.49%
Pb	T-107	26.0	30.0	0.2	0.66	15.65%
Pb	T-109	34.9	39.3	1.2	3.0	12.69%
Sb	WP980-1	16.9	18.3	0.47	2.6	8.27%
Sb	WP980-2	101.5	108.9	34.4	31.6	7.33%
Se	T-95	60.1	65.9	2.6	3.94	9.77%
Se	T-107	11.0	13.0	0.9	6.9	19.00%
Tl	WP980-1	50.0	55.1	2	3.6	10.26%
Tl	WP980-2	6.3	7.0	0.52	7.4	11.66%
V	Tm-11	491.0	532.6	26.1	4.9	8.48%
V	Tm-12	2319.0	2412.8	60.6	2.5	4.05%
Be	T-107	11.0	11.3	0.53	4.7	3.00%
Be	T-109	22.1	25.6	0.91	3.6	15.97%
Ca	T-107	11700.0	12364.0	783.6	6.3	5.68%
Ca	T-109	35400.0	38885.0	999	2.6	9.84%

TABLE 1 (continued)

Elem	Material	Certified Mean	Observed Mean	Std. Dev.	Relative Standard Deviation	Relative Bias
Ca	T-107	11700.0	12364.0	783.6	6.3	5.68%
Ca	T-109	35400.0	38885.0	999	2.6	9.84%
Mg	T-95	32800.0	35002.0	1900	5.4	6.71%
Mg	T-107	2100.0	2246.7	110.5	4.9	6.99%
Mg	T-109	9310.0	10221.7	218.6	2.1	9.79%
Na	T-95	190000.0	218130.0	10700	4.9	14.81%
Na	T-107	20700.0	22528.0	1060	4.7	8.83%
Na	T-109	12000.0	13799.5	516.2	3.7	15.00%
Cr	Tm-11	52.1	64.3	4.1	6.4	23.51%
Cr	Tm-12	299.0	346.0	9.8	2.8	15.74%
Cr	T-107	13.0	22.3	1.5	6.7	71.77%
Cr	T-109	18.7	32.6	6.4	19.6	74.71%
Cu	Tm-11	46.3	76.5	4.4	5.7	65.36%
Cu	Tm-12	288.0	324.0	8.9	2.7	12.52%
Cu	T-107	30.0	42.3	4.0	9.4	41.17%
Cu	T-109	21.4	54.0	3.6	6.7	152.38%
Fe	Tm-11	249.0	289.3	16.4	5.7	16.18%
Fe	Tm-12	1089.0	1182.5	43.5	3.7	8.59%
Fe	T-107	52.0	63.8	8.7	13.6	22.69%
Fe	T-109	106.0	134.0	6.6	4.9	26.50%
Mn	Tm-11	46.0	60.9	3.2	5.2	32.48%
Mn	Tm-12	263.0	304.4	9.1	3.0	15.77%
Mn	T-107	45.0	52.6	3.1	5.9	17.09%
Mn	T-109	34.0	46.6	3.0	6.4	37.18%
Ag	WS378-1	46.0	19.4	5.6	2.9	-57.83%


Start
7.1 Calibrate the microwave equipment.
7.2 Acid wash and H_2O rinse all digestion vessels and glassware.
7.3.2 Measure 45 mL aliquot into the digestion vessel.
7.3.3 Use blank samples of reagent H_2O in other digestion vessels.
7.3.4 Add concentrated HNO_3 to each vessel.
7.3.5 Place vessels in the carousel; use blanks if necessary to balance power.
7.3.6 Place the carousel in oven, heat according to power program.
7.3.7 Allow samples to cool so they are not hot to touch.
7.3.8 Place sample in acid-cleaned bottle.
Are particulates present?
Yes
7.3.8 - 7.3.8.3 Centrifuge, settle, and filter sample.
No
7.3.9 Correct concentration values for the dilution factor.
Stop

METHOD 3020A

ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS FOR TOTAL METALS FOR ANALYSIS BY GFAA SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for analysis by furnace atomic absorption spectroscopy (GFAA) for the metals listed below. The procedure is used to determine the total amount of the metal in the sample.

1.2 Samples prepared by Method 3020 may be analyzed by GFAA for the following metals:

Beryllium	Lead
Cadmium	Molybdenum
Chromium	Thallium
Cobalt	Vanadium

NOTE: For the digestion and GFAA analysis of arsenic and selenium, see Methods 7060 and 7740. For the digestion and GFAA analysis of silver, see Method 7761.

2.0 SUMMARY OF METHOD

2.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is cooled and brought up in dilute nitric acid such that the final dilution contains 3% (v/v) nitric acid. This percentage will vary depending on the amount of acid used to complete the digestion. If the sample contains suspended solids, it must be centrifuged, filtered, or allowed to settle.

3.0 INTERFERENCES

3.1 Interferences are discussed in the referring analytical method.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers - 150-mL, or equivalent.

4.2 Watch glasses - ribbed or equivalent.

4.3 Qualitative filter paper or centrifugation equipment.

4.4 Funnel or equivalent.

4.5 Graduated Cylinder - 100mL.

4.6 Electric hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95°C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine levels of impurities. If method blank is < MDL, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3, for further information.

6.3 Aqueous wastewaters must be acidified to a pH of < 2 with HNO_3.

7.0 PROCEDURE

7.1 Transfer a 100-mL representative aliquot of the well-mixed sample to a 150-mL Griffin beaker and add 3 mL of concentrated HNO_3. Cover the beaker with a ribbed watch glass. Place the beaker on a hot plate and cautiously evaporate to a low volume (5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3-mL portion of concentrated HNO_3. Cover the beaker with a non-ribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

7.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). When the digestion is complete, evaporate to a low volume (3 mL); use a ribbed watch glass, not allowing any portion of the bottom of the beaker to go dry. Remove the beaker and add approximately 10 mL of water, mix, and continue warming the beaker for 10 to 15 minutes to allow additional solubilization of any residue to occur.

7.3 Remove the beaker from the hot plate and wash down the beaker walls and watch glass with water. When necessary, filter or centrifuge the sample to remove silicates and other insoluble material that may interfere with injecting the sample into the graphite atomizer. (This additional step can cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO_3.) Adjust to the final volume of 100 mL with water. The sample is now ready for analysis.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each batch of samples processed, method blanks should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. Replicate samples will be used to determine precision. The sample load will dictate frequency, but 5% is recommended. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each batch of samples processed or 5% and whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spikes.

8.5 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source. Refer to Chapter One for the proper protocol.

8.6 The method of standard addition shall be used for the analysis of all EP extracts. See Method 7000, Step 8.7, for further information.

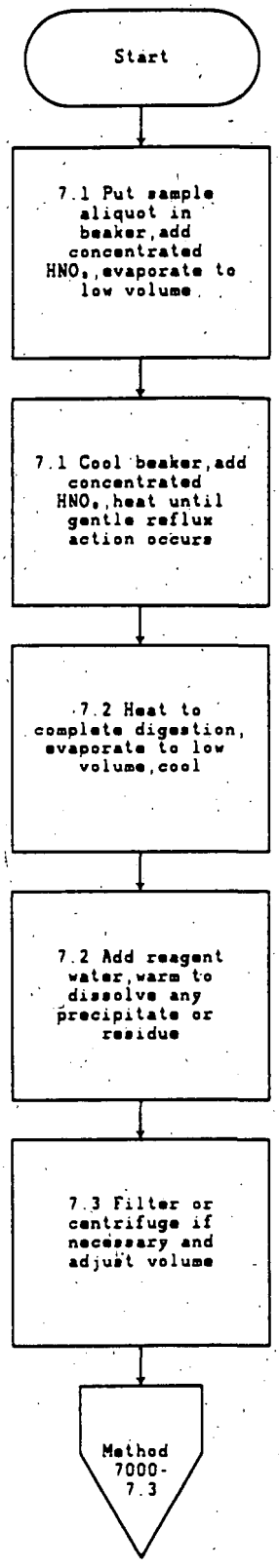
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.


Start
7.1 Put sample aliquot in beaker, add concentrated HNO_3, evaporate to low volume
7.1 Cool beaker, add concentrated HNO_3, heat until gentle reflux action occurs
7.2 Heat to complete digestion, evaporate to low volume, cool
7.2 Add reagent water, warm to dissolve any precipitate or residue
7.3 Filter or centrifuge if necessary and adjust volume
Method 7000-7.3

METHOD 3050A

ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

1.0 SCOPE AND APPLICATION

1.1 This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (FLAA and GFAA, respectively) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by ICP for all the listed metals, or by FLAA or GFAA as indicated below (see also Step 2.1):

FLAA		GFAA
Aluminum	Magnesium	Arsenic
Barium	Manganese	Beryllium
Beryllium	Molybdenum	Cadmium
Cadmium	Nickel	Chromium
Calcium	Osmium	Cobalt
Chromium	Potassium	Iron
Cobalt	Silver	Lead
Copper	Sodium	Molybdenum
Iron	Thallium	Selenium
Lead	Vanadium	Thallium
	Zinc	Vanadium

NOTE: See Method 7760 for FLAA preparation for Silver.

2.0 SUMMARY OF METHOD

2.1 A representative 1- to 2-g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used for flame AA and ICP analyses and nitric acid is used for furnace AA work. Dilute hydrochloric acid is used as the final reflux acid for (1) the ICP analysis of As and Se, and (2) the flame AA or ICP analysis of Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Os, Pb, Tl, V, and Zn. Dilute nitric acid is employed as the final dilution acid for the furnace AA analysis of As, Be, Cd, Cr, Co, Fe, Pb, Mo, Se, Tl, and V. The diluted samples have an approximate acid concentration of 5.0% (v/v). A separate sample shall be dried for a total % solids determination.

3.0 INTERFERENCES

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method 3050 is applicable to a given waste.

4.0 APPARATUS AND MATERIALS

4.1 Conical Phillips beakers - 250-mL, or equivalent.

4.2 Watch glasses ribbed or equivalent.

4.3 Drying ovens - That can be maintained at 30° C.

4.4 Thermometer - That covers range of 0-200°C.

4.5 Filter paper - Whatman No. 41 or equivalent.

4.6 Centrifuge and centrifuge tubes.

4.7 Analytical Balance - Capable of accurately weighing to the nearest 0.01 g.

4.8 Electric Hot Plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.9 Glass Funnel or equivalent.

4.10 Graduated cylinder or equivalent.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrogen peroxide (30%), H_2O_2. Oxidant should be analyzed to determine level of impurities.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3, for further information.

6.3 Nonaqueous samples shall be refrigerated upon receipt and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh to the nearest 0.01 g and transfer to a conical beaker 1.00-2.00 g of sample. For samples with low percent solids a larger sample size may be used as long as digestion is completed.

7.2 Add 10 mL of 1:1 HNO_3, mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the watch glass, and reflux for 30 minutes. Repeat this last step to ensure complete oxidation. Using a ribbed watch glass, allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker.

7.3 After Step 7.2 has been completed and the sample has cooled, add 2 mL of water and 3 mL of 30% H_2O_2. Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the beaker.

7.4 Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

<u>NOTE</u>: Do not add more than a total of 10 mL 30% H_2O_2.

7.5 If the sample is being prepared for (a) the ICP analysis of As and Se, or (b) the flame AA or ICP analysis of Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Os, Pb, Tl, V, and Zn, then add 5 mL of concentrated HCl and 10 mL of water, return the covered beaker to the hot plate, and reflux for an additional 15 minutes without boiling. After cooling, dilute to a 100 mL volume with water. Particulates in the digestate that may clog the nebulizer should be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.5.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent).

7.5.2 Centrifugation - Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.5.3 The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5.0% (v/v) HNO_3. The sample is now ready for analysis.

7.6 If the sample is being prepared for the furnace analysis of As, Be, Cd, Co, Cr, Fe, Mo, Pb, Se, Tl, and V, cover the sample with a ribbed watch glass and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL. After cooling, dilute to 100 mL with water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.6.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent).

7.6.2 Centrifugation - Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.6.3 The diluted digestate solution contains approximately 5% (v/v) HNO_3. For analysis, withdraw aliquots of appropriate volume and add any required reagent or matrix modifier. The sample is now ready for analysis.

7.7 Calculations

7.7.1 The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

7.7.2 If percent solids is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each batch of samples processed, preparation blanks should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. Replicate samples will be used to determine precision. The sample load will dictate frequency, but 5% is recommended. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials must be employed to determine accuracy. A spiked sample should be included with each batch of

samples processed and whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spikes.

8.5 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

9.0 METHOD PERFORMANCE

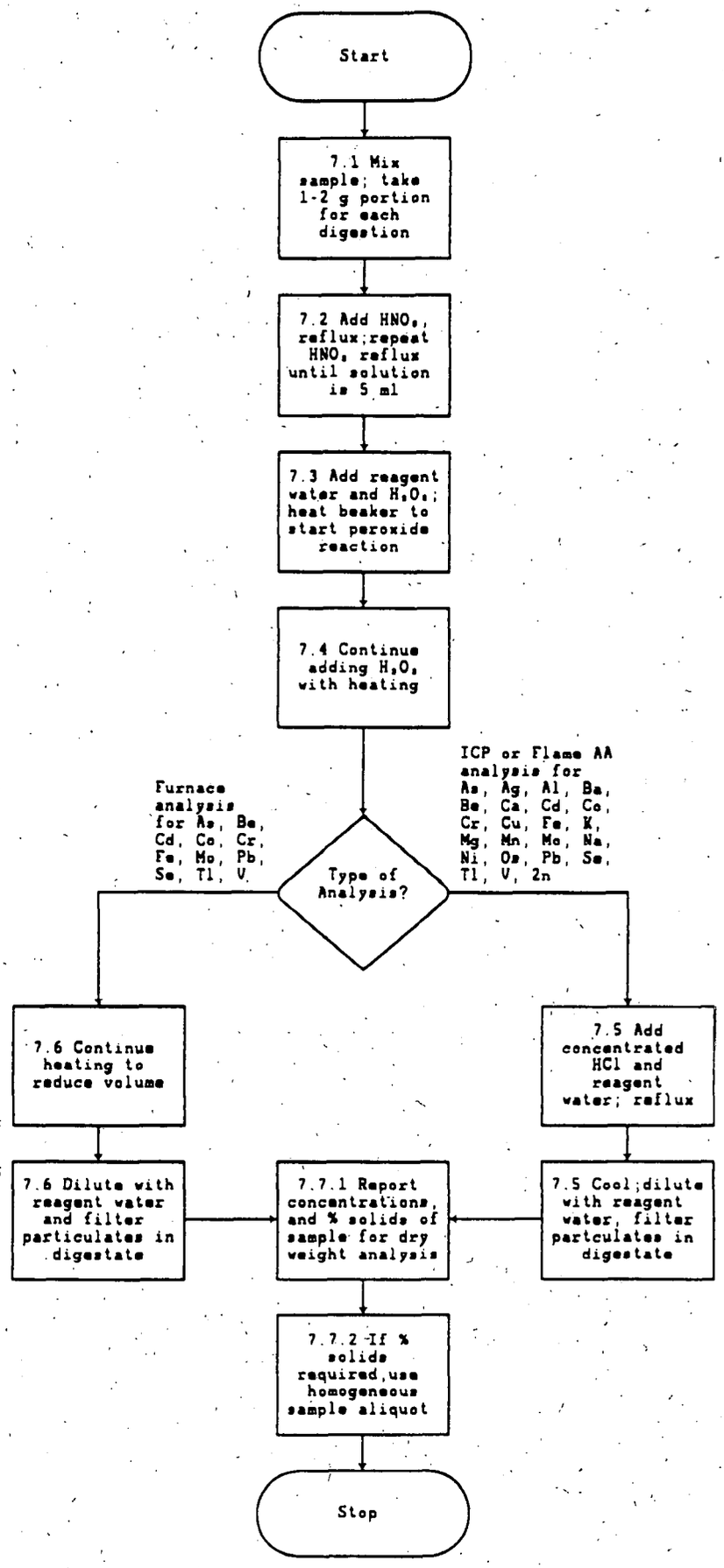
9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

3. Edgell, K.; USEPA Method Study 37 - SW-846 Method 3050 Acid Digestion of Sediments, Sludges, and Soils. EPA Contract No. 68-03-3254, November 1988.


Start
7.1 Mix sample; take 1-2 g portion for each digestion
7.2 Add HNO_3, reflux;repeat HNO_3 reflux until solution is 5 ml
7.3 Add reagent water and H_2O_2; heat beaker to start peroxide reaction
7.4 Continue adding H_2O_2 with heating
Type of Analysis?
Furnace analysis for As, Be, Cd, Co, Cr, Fe, Mo, Pb, Se, Tl, V.
ICP or Flame AA analysis for As, Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Os, Pb, Se, Tl, V, Zn
7.6 Continue heating to reduce volume
7.5 Add concentrated HCl and reagent water; reflux
7.6 Dilute with reagent water and filter particulates in digestate
7.7.1 Report concentrations, and % solids of sample for dry weight analysis
7.5 Cool;dilute with reagent water, filter particulates in digestate
7.7.2 If % solids required,use homogeneous sample aliquot
Stop

METHOD 3051

MICROWAVE ASSISTED ACID DIGESTION OF SEDIMENTS, SLUDGES, SOILS, AND OILS

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the microwave assisted acid digestion of sludges, sediments, soils, and oils for the following elements:

Aluminum	Cadmium	Iron	Molybdenum	Sodium
Antimony	Calcium	Lead	Nickel	Strontium
Arsenic	Chromium	Magnesium	Potassium	Thallium
Boron	Cobalt	Manganese	Selenium	Vanadium
Barium	Copper	Mercury	Silver	Zinc
Beryllium				

1.2 This method is provided as an alternative to Method 3050. It is intended to provide a rapid multielement acid leach digestion prior to analysis so that decisions can be made about site cleanup levels, the need for TCLP testing of a waste and whether a BDAT process is providing acceptable performance. If a decomposition including hydrochloric acid is required for certain elements, it is recommended that Method 3050A be used. Digests produced by the method are suitable for analysis by flame atomic absorption (FLAA), graphite furnace atomic absorption (GFAA), inductively coupled plasma emission spectroscopy (ICP-ES) and inductively coupled plasma mass spectrometry (ICP-MS). Due to the rapid advances in microwave technology, consult your manufacturer's recommended instructions for guidance on their microwave digestion system and refer to the SW-846 "DISCLAIMER" when conducting analyses using Method 3051.

2.0 SUMMARY OF METHOD

2.1 A representative sample of up to 0.5 g is digested in 10 mL of concentrated nitric acid for 10 min using microwave heating with a suitable laboratory microwave unit. The sample and acid are placed in a fluorocarbon (PFA or TFM) microwave vessel. The vessel is capped and heated in the microwave unit. After cooling, the vessel contents are filtered, centrifuged, or allowed to settle and then diluted to volume and analyzed by the appropriate SW-846 method (Ref. 1).

3.0 INTERFERENCES

3.1 Very reactive or volatile materials that may create high pressures when heated may cause venting of the vessels with potential loss of sample and analytes. The complete decomposition of either carbonates, or carbon based samples, may cause enough pressure to vent the vessel if the sample size is greater than 0.25 g when used in the 120 mL vessels with a pressure relief device that has an upper limit of 7.5± 0.7 atm (110 ± 10 psi).

4.0 APPARATUS AND MATERIALS

4.1 Microwave apparatus requirements.

4.1.1 The microwave unit provides programmable power with a minimum of 574 W, which can be programmed to within ± 10 W of the required power. Typical units provide a nominal 600 W to 1200 W of power. Pressure, or especially temperature, monitoring and control of the microwave unit are desirable.

4.1.2 The microwave unit cavity is corrosion resistant and well ventilated.

4.1.3 All electronics are protected against corrosion for safe operation.

4.1.4 The system requires fluorocarbon (PFA or TFM) digestion vessels (120 mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psi) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psi).

4.1.5 A rotating turntable is employed to insure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.

> CAUTION: Those laboratories now using or contemplating the use of kitchen type microwave ovens for this method should be aware of several signifant safety issues. First, when an acid such as nitric is used to assist sample digestion in microwave units in open vessels, or sealed vesselsequippedres, there is the potential for the acid gases released to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened. This can result in operator exposure to microwave energy. Use of a unit with corrosion resistant safety devices prevents this from occurring.
>
> CAUTION: The second safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures but must be safely contained. However, many digestion vessels constructed from certain fluorocarbons may crack, burst, or explode in the unit under certain pressures. Only unlined fluorocarbon (PFA or TFM) containers with pressure relief mecahnisms or containers with PFA-fluorocarbon liners and pressure relief mechanisms are considered acceptable at present.
>
> Users are therefore advised not to use kitchen type microwave ovens or to use sealed containers without pressure relief

valves for microwave acid digestions by this method. Use of laboratory-grade microwave equipment is required to prevent safety hazards. For further details consult reference 2.

CAUTION: There are many safety and operational recommendations specific to the model and manufacturer of the microwave equipment used in individual laboratories. These specific suggestions are beyond the scope of this method and require the analyst to consult the specific equipment manual, manufacturer and literature for proper and safe operation of the microwave equipment and vessels.

4.2 Volumetric graduated cylinder, 50 or 100 mL capacity or equivalent.

4.3 Filter paper, qualitative or equivalent.

4.4 Filter funnel, glass or disposable polypropylene.

4.5 Analytical balance, 300 g capacity, and minimum ± 0.01 g.

5.0 REAGENTS

5.1 All acids should be sub-boiling distilled where possible to minimize the blank levels due to metallic contamination. Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.1.1 Concentrated nitric acid, HNO_3. Acid should be analyzed to determine levels of impurity. If the method blank is less than the MDL, the acid can be used.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified (Ref. 3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids and water. Plastic and glass containers are both suitable. See Chapter Three, sec. 3.1.3 of this manual, for further information.

6.3 Samples must be refrigerated upon receipt and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Calibration of Microwave Equipment

NOTE: If the microwave unit uses temperature feedback control capable of replicating the performance specifications of the method, then the calibration procedure may be omitted.

7.1.1 Measurement of the available power for heating is evaluated so that absolute power in watts may be transferred from one microwave unit to another. For cavity type microwave equipment, this is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the unit. The calibration format required for laboratory microwave units depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few units have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a three-point calibration method (7.1.3), otherwise, the analyst must use the multiple point calibration method (7.1.2).

7.1.2 The multiple point calibration involves the measurement of absorbed power over a large range of power settings. Typically, for a 600 W unit, the following power settings are measured; 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% using the procedure described in section 7.1.4. This data is clustered about the customary working power ranges. Nonlinearity has been commonly encountered at the upper end of the calibration. If the unit's electronics are known to have nonlinear deviations in any region of proportional power control, it will be necessary to make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. This setting should be checked periodically to evaluate the integrity of the calibration. If a significant change is detected (±10 W), then the entire calibration should be reevaluated.

7.1.3 The three-point calibration involves the measurement of absorbed power at three different power settings. Measure the power at 100% and 50% using athe procedure described in section 7.1.4. From the 2-point line calculate the power setting corresponding to the required power in watts specified in the procedure. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power within ±10 W, use the multiple point calibration in 7.1.2. This point should also be used to periodically verify the integrity of the calibration.

7.1.4 Equilibrate a large volume of water to room temperature (23 ± 2°C). One kg of reagent water is weighed (1,000.0 g ± 0.1 g) into a fluorocarbon beaker or a beaker made of some other material that does not significantly absorb microwave energy (glass absorbs microwave energy and is not recommended). The initial temperature of the water should be

23 ± 2°C measured to ± 0.05°C. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the unit's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation and record the maximum temperature within the first 30 seconds to ± 0.05°C. Use a new sample for each additional measurement. If the water is reused both the water and the beaker must have returned to 23 ± 2°C. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship:

Eq. 1
$$P = \frac{(K)\ (C_p)\ (m)\ (\Delta T)}{t}$$

Where:

P = the apparent power absorbed by the sample in watts (W) ($W = joule \cdot sec^{-1}$)

K = the conversion factor for thermochemical $calories \cdot sec^{-1}$ to watts (=4.184)

C_p = the heat capacity, thermal capacity, or specific heat ($cal \cdot g^{-1} \cdot °C^{-1}$) of water

m = the mass of the water sample in grams (g)

ΔT = the final temperature minus the initial temperature (°C)

t = the time in seconds (s)

Using the experimental conditions of 2 minutes and 1 kg of distilled water (heat capacity at 25 °C is 0.9997 $cal \cdot g^{-1} \cdot °C^{-1}$) the calibration equation simplifies to:

Eq. 2
$$P = (\Delta T)\ (34.86)$$

<u>NOTE</u>: Stable line voltage is necessary for accurate and reproducible calibration and operation. The line voltage should be within manufacturer's specification, and during measurement and operation should not vary by more than ±2 V. A constant power supply may be necessary for microwave use if the source of the line voltage is unstable.

Electronic components in most microwave units are matched to the units' function and output. When any part of the high voltage

circuit, power source, or control components in the unit have been serviced or replaced, it will be necessary to recheck the units' calibration. If the power output has changed significantly (±10 W), then the entire calibration should be reevaluated.

7.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between high concentration samples and low concentration samples, all digestion vessels should be cleaned by leaching with hot (1:1) hydrochloric acid (greater than 80°C, but less than boiling) for a minimum of two hours followed with hot (1:1) nitric acid (greater than 80°C, but less than boiling) for a minimum of two hours and rinsed with reagent water and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric or glass volumetric ware and storage containers should be cleaned by leaching with more dilute acids (approximately 10% V/V) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment. To avoid precipitation of silver, ensure that all HCl has been rinsed from the vessels.

7.3 Sample Digestion

7.3.1 Weigh the fluorocarbon (PFA or TFM) digestion vessel, valve and capassembly to 0.001 g prior to use.

7.3.2 Weigh a well-mixed sample to the nearest 0.001 g into the fluorocarbon sample vessel equipped with a single-ported cap and a pressure relief valve. For soils, sediments, and sludges use no more than 0.500 g. For oils use no more than 0.250 g.

7.3.3 Add 10 ± 0.1 mL concentrated nitric acid in a fume hood. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel. Cap the vessel and torque the cap to 12 ft-lbs (16 N-m) or according to the unit manufacturer's directions. Weigh the vessels to the nearest 0.001 g. Place the vessels in the microwave carousel.

<u>CAUTION</u>: Toxic nitrogen oxide fumes may be evolved, therefore all work must be performed in a properly operating ventilation system. The analyst should also be aware of the potential for a vigorous reaction. If a vigorous reaction occurs, allow to cool before capping the vessel.

<u>CAUTION</u>: When digesting samples containing volatile or easily oxidized organic compounds, initially weigh no more than 0.10 g and observe the reaction before capping the vessel. If a vigorous reaction occurs, allow the reaction to cease before capping the vessel. If no appreciable reaction occurs, a sample weight up to 0.25 g can be used.

CAUTION: All samples known or suspected of containing more than 5-10% organic material should be predigested in a hood for at least 15 minutes.

7.3.4 Properly place the carousel in the microwave unit according to the manufacturer's recommended specifications and, if used, connect the pressure vessels to the central overflow vessel with PFA-fluorocarbon tubes. Any vessels containing 10 mL of nitric acid for analytical blank purposes are counted as sample vessels. When fewer than the recommended number of samples are to be digested, the remaining vessels should be filled with 10 mL of nitric acid to achieve the full complement of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity (Ref. 4). Irradiate each group of sample vessels for 10 minutes. The temperature of each sample should rise to 175 °C in less than 5.5 minutes and remain between 170-180 °C for the balance of the 10 minute irradiation period. The pressure should peak at less than 6 atm for most soil, sludge, and sediment samples (Ref. 5). The pressure will exceed these limits in the case of high concentrations of carbonate or organic compounds. In these cases the pressure will be limited by the relief pressure of the vessel to 7.5 ± 0.7 atm (110 ± 10 psi). All vessels should be sealed according to the manufacturers recommended specifications.

7.3.4.1 Newer microwave units are capable of higher power (W) that permits digestion of a larger number of samples per batch. If the analyst wishes to digest more samples at a time, the analyst may use different values of power as long as they result in the same time and temperature conditions defined in 7.3.4. That is, any sequence of power that brings the samples to 175°C in 5.5 minutes and permits a slow rise to 175 - 180°C during the remaining 4.5 minutes (Ref. 5).

Issues of safety, structural integrity (both temperature and pressure limitations), heat loss, chemical compatibility, microwave absorption of vessel material, and energy transport will be considerations made in choosing alternative vessels. If all of the considerations are met and the appropriate power settings provided to reproduce the reaction conditions defined in 7.3.4, then these alternative vessels may be used (Ref. 1,2).

7.3.5 At the end of the microwave program, allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave unit. When the vessels have cooled to room temperature, weigh and record the weight of each vessel assembly. If the weight of acid plus sample has decreased by more than 10 percent from the original weight, discard the sample. Determine the reason for the weight loss. These are typically attributed to loss of vessel seal integrity, use of a digestion time longer than 10 minutes, too large a sample, or improper heating conditions. Once the source of the loss has been corrected, prepare a new sample or set of samples for digestion beginning at 7.3.1.

7.3.6 Complete the preparation of the sample by carefully uncapping and venting each vessel in a fume hood. Transfer the sample to an acid-cleaned bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, the sample may be centrifuged, allowed to settle, or filtered.

7.3.6.1 Centrifugation: Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.3.6.2 Settling: Allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

7.3.6.3 Filtering: The filtering apparatus must be thoroughly cleaned and prerinsed with dilute (approximately 10% V/V) nitric acid. Filter the sample through qualitative filter paper into a second acid-cleaned container.

7.3.7 Dilute the digest to a known volume ensuring that the samples and standards are matrix matched. The digest is now ready for analysis for elements of interest using the appropriate SW-846 method.

7.4 Calculations: The concentrations determined are to be reported on the basis of the actual weight of the original sample.

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period of three years. This method is restricted to use by, or under supervision of, experienced analysts. Refer to the appropriate section of Chapter One for additional quality control guidance.

8.2 Duplicate samples should be processed on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analytical process. A duplicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number. A duplicate sample should be prepared for each matrix type (i.e., soil, sludge, etc.).

8.3 Spiked samples or standard reference materials should be included with each group of samples processed or every 20 samples, whichever is the greater number. A spiked sample should also be included whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision: Precision data for Method 3051, as determined by the statistical examination of interlaboratory test results, is located in Tables 1 and 2.

9.2 Repeatability: If successive results are obtained by the same analyst with the same apparatus under constant operating conditions on identical test material, then the difference between these successive results will not, with 95% probability, exceed the repeatability value. For example, in the case of lead, an average of only 1 case in 20 would exceed

$$0.206\ x$$

in the long run, where x is one result in μg/g (Ref. 6).

9.3 Reproducibility: If two successive measurements are made independently by each of two different analysts working in different laboratories on identical test material, then the difference between the average result for each analyst will not, with 95% probability, exceed the reproducibility value. For example, in the case of lead, an average of only 1 case in 20 would exceed

$$0.303\ x$$

in the long run, where x is the average of two successive measurements in μg/g (Ref. 2).

As can be seen in Table 1, repeatability and reproducibility differ between elements, and usually depend on that element's concentration. Table 2 provides an example of how users of the method can determine expected values for repeatability and reproducibility; nominal values of lead have been used for this model (Ref. 6).

9.4 Bias: In the case of SRM 1085 - Wear Metals in Oil, the bias of this test method is different for each element. An estimate of bias, as shown in Table 3, is:

Bias = Amount found - Amount expected.

However, the bias estimate inherits both the uncertainty in the measurements made using Method 3051 and the uncertainty on the certificate, so whether the bias is real or only due to measurement error must also be considered. The concentrations found for Al, Cr, and Cu using Method 3051 fall within their certified ranges on SRM 1085, and 95% confidence intervals for Fe and Ni overlap with their respective certified ranges; therefore, the observed biases for these elements are probably due to chance and should be considered insignificant. Biases should not be estimated at all for Ag and Pb because these elements were not certified. Therefore, the only two elements considered in this table for which the bias estimates are significant are Mg and Mo.

10.0 REFERENCES

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TABLE 1.
EQUATIONS RELATING REPEATABILITY AND REPRODUCIBILITY TO MEAN CONCENTRATION OF DUPLICATE DETERMINATION WITH 95 PERCENT CONFIDENCE

Element	Repeatability	Reproducibility
Ag	0.195X[a]	0.314X
Al	0.232X	0.444X
B	12.9[b]	22.6[b]
Ba	0.238X	0.421X
Be	0.082[b]	0.082[b]
Ca	0.356X	1.27X
Cd	0.385X	0.571X
Co	0.291X	0.529X
Cr	0.187X	0.195X
Cu	0.212X	0.322X
Fe	0.257X	0.348X
Mg	0.238X	0.399X
Mn	1.96X1/2[c]	4.02X1/2
Mo	0.701X	0.857X
Ni	0.212X	0.390X
Pb	0.206X	0.303X
Sr	0.283X	0.368X
V	1.03X1/2	2.23X1/2
Zn	3.82X1/2	7.69X1/2

[a]Log transformed variable based on one-way analysis of variance.
[b]Repeatability and reproducibility were independent of concentration.
[c]Square root transformed variable based on one-way analysis of variance.

TABLE 2.
REPEATABILITY AND REPRODUCIBILITY FOR LEAD
BY METHOD 3051

Average Value	Repeatability	Reproducibility
50	10.3	15.2
100	20.6	30.3
200	41.2	60.6
300	61.8	90.9
400	82.4	121
500	103	152

All results are in mg/Kg

TABLE 3.
RECOVERY AND BIAS DATA FOR SRM 1085 - WEAR METALS IN OIL

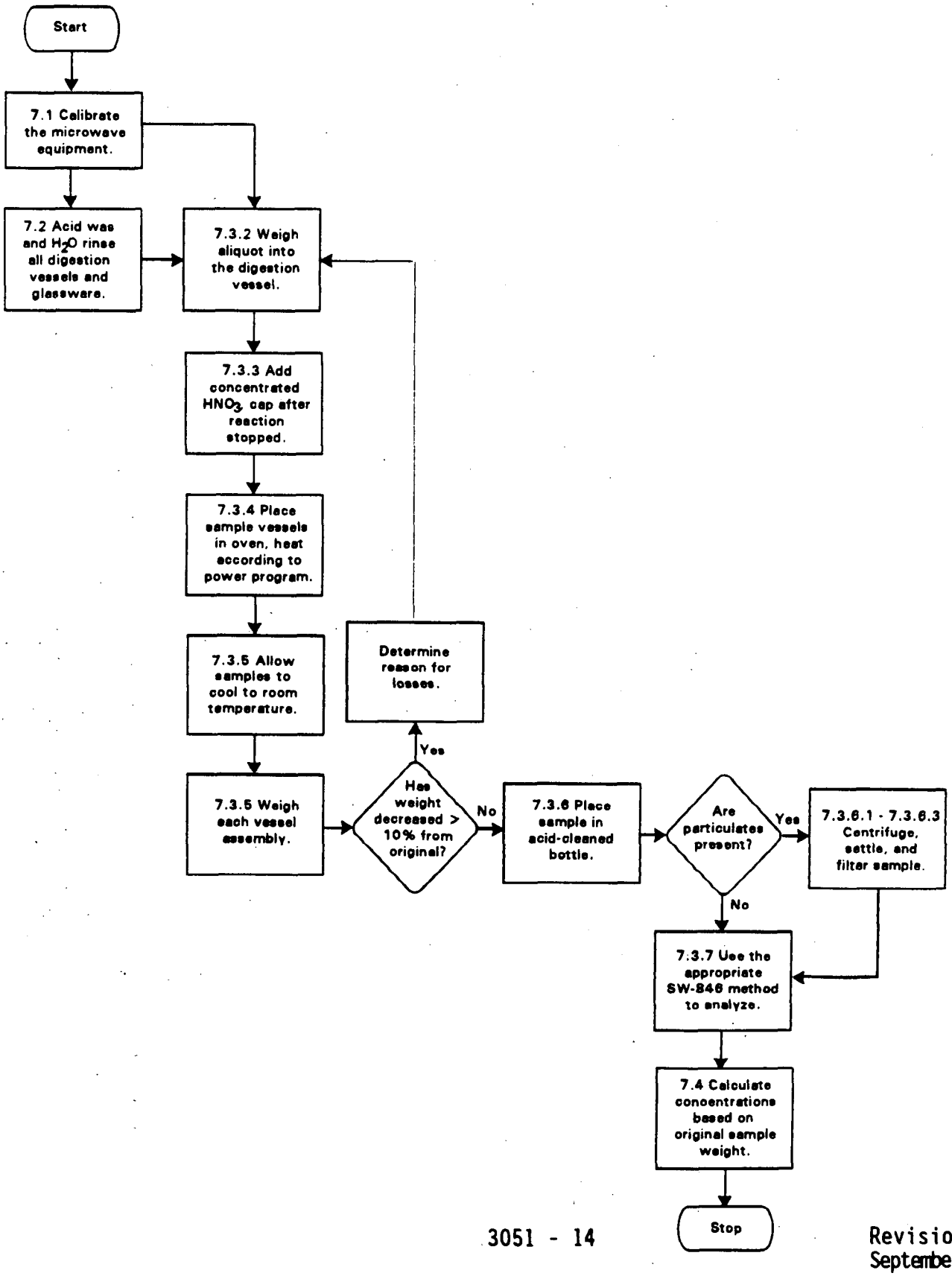
Element	Amount Expected (Certified Range)	Amount Found* (95% Conf Interval)	Absolute Bias (μg/g)	Relative Bias (Percent)	Significant (due to more than chance)
Ag	(291)**	234±16	--	--	--
Al	296±4	295±12	-1	0	No
Cr	298±5	293±10	-5	-2	No
Cu	295±10	289±9	-6	-2	No
Fe	300±4	311±14	+11	+4	No
Mg	297±3	270±11	-27	-9	Yes
Mo	292±11	238±11	-54	-18	Yes
Ni	303±7	293±9	-10	-3	No
Pb	(305)**	279±8	--	--	--

All values in mg/Kg

*Results taken from table 4-7, Ref. 2.

**Value not certified, so should not be used in bias detection and estimation.

METHOD 3051
(MICROWAVE ASSISTED ACID DIGESTION OF SEDIMENTS, SLUDGES, SOILS, AND OILS)



3500A

METHOD 3500A

ORGANIC EXTRACTION AND SAMPLE PREPARATION

1.0 SCOPE AND APPLICATION

1.1 The 3500 Methods are procedures for quantitatively extracting nonvolatile and semivolatile organic compounds from various sample matrices. Cleanup and/or analysis of the resultant extracts are described in Chapter Two, Sections 2.3.2 and 2.3.1, respectively.

1.2 Method 3580 describes a solvent dilution technique that may be used on non-aqueous nonvolatile and semivolatile organic samples prior to cleanup and/or analysis.

1.3 The 5000 Methods are procedures for preparing samples containing volatile organic compounds for quantitative analysis.

1.4 Refer to the specific method of interest for further details.

2.0 SUMMARY OF METHOD

2.1 3500 Methods: A sample of a known volume or weight is solvent extracted. The resultant extract is dried and then concentrated in a Kuderna-Danish apparatus (if necessary). Other concentration devices or techniques may be used in place of the Kuderna-Danish concentrator if the quality control requirements of the determinative methods are met (Method 8000, Section 8.0).

2.2 5000 Methods: Refer to the specific method of interest.

3.0 INTERFERENCES

3.1 Samples requiring analysis for volatile organic compounds, can be contaminated by diffusion of volatile organics (particularly chlorofluoro-carbons and methylene chloride) through the sample container septum during shipment and storage. A field blank prepared from organic-free reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.2 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Refer to Chapter One for specific guidance on quality control procedures.

3.3 Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary. Refer to Method 3600 for guidance on cleanup procedures.

3.4 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

3.5 Glassware contamination resulting in analyte degradation: Soap residue on glassware may cause degradation of certain analytes. Specifically, aldrin, heptachlor, and most organophosphorus pesticides will degrade in this situation. This problem is especially pronounced with glassware that may be difficult to rinse (e.g., 500 mL K-D flask). These items should be hand-rinsed very carefully to avoid this problem.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific method of interest for a description of the apparatus and materials needed.

5.0 REAGENTS

5.1 Refer to the specific method of interest for a description of the solvents needed.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water as defined in Chapter One.

5.3 Stock standards: Stock solutions may be prepared from pure standard materials or purchased as certified solutions.

5.3.1 Purgeable stock standards: Prepare stock standards in methanol using assayed liquids or gases, as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood.

5.3.1.1 Place about 9.8 mL of methanol in a 10-mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.3.1.2 Using a 100-µL syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.3.1.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.1.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

5.3.1.5 All standards must be replaced after 1 month, or sooner if comparison with check standards indicates a problem.

5.3.2 Semivolatile stock standards: Base/neutral and acid stock standards are prepared in methanol. Organochlorine pesticide standards are prepared in acetone.

5.3.2.1 Stock standard solutions should be stored in Teflon-sealed containers at 4°C. The solutions should be checked frequently for stability. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicate a problem.

5.4 Surrogate standards: A surrogate standard (i.e., a chemically inert compound not expected to occur in an environmental sample) should be added to each sample, blank, and matrix spike sample just prior to extraction or processing. The recovery of the surrogate standard is used to monitor for unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within the acceptance limits. Recommended surrogates for different analyte groups follow. However, these compounds, or others that better correspond to the analyte group, may be used for other analyte groups as well. Normally three or more standards are added for each analyte group.

5.4.1 Base/neutral and acid surrogate spiking solutions: The following are recommended surrogate standards.

Base/neutral	Acid
2-Fluorobiphenyl	2-Fluorophenol
Nitrobenzene-d_5	2,4,6-Tribromophenol
Terphenyl-d_{14}	Phenol-d_6

5.4.1.1 Prepare a surrogate standard spiking solution in methanol that contains the base/neutral compounds at a concentration of 100 mg/L, and the acid compounds at 200 mg/L for water and sediment/soil samples (low- and medium-level). For waste samples, the concentration should be 500 mg/L for base/neutrals and 1000 mg/L for acids.

5.4.2 Organochlorine pesticide/PCB surrogate spiking solution: The following are recommended surrogate standards for organochlorine pesticides/PCBs.

Organochlorine pesticides/PCBs

Dibutylchlorendate (DBC) (if available)
2,4,5,6-Tetrachloro-meta-xylene (TCMX)

5.4.2.1 Prepare a surrogate standard spiking solution at a concentration of 1 mg/L in acetone for water and sediment/soil samples. For waste samples, the concentration should be 5 mg/L.

5.4.3 Purgeable surrogate spiking solution: The following are recommended surrogate standards for volatile organics.

Purgeable organics

p-Bromofluorobenzene
1,2-Dichloroethane-d_4
Toluene-d_8

5.4.3.1 Prepare a surrogate spiking solution (as described in Section 5.3.1 or through secondary dilution of the stock standard) in methanol containing the surrogate standards at a concentration of 25 mg/L.

5.5 Matrix spike standards: Select five or more analytes from each analyte group for use in a spiking solution. The following are recommended matrix spike standard mixtures for a few analyte groups. These compounds, or others that better correspond to the analyte group, may be used for other analyte groups as well.

5.5.1 Base/neutral and acid matrix spiking solution: Prepare a spiking solution in methanol that contains each of the following base/neutral compounds at 100 mg/L and the acid compounds at 200 mg/L for water and sediment/soil samples. The concentration of these compounds should be five times higher for waste samples.

Base/neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

5.5.2 Organochlorine pesticide matrix spiking solution: Prepare a spiking solution in acetone or methanol that contains the following pesticides in the concentrations specified for water and sediment/soil. The concentration should be five times higher for waste samples.

Pesticide	Concentration (mg/L)
Lindane	0.2
Heptachlor	0.2
Aldrin	0.2
Dieldrin	0.5
Endrin	0.5
4,4'-DDT	0.5

5.5.3 Purgeable matrix spiking solution: Prepare a spiking solution in methanol that contains the following compounds at a concentration of 25 mg/L.

Purgeable organics

1,1-Dichloroethene
Trichloroethene
Chlorobenzene
Toluene
Benzene

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to the Organic Analyte Chapter, Section 4.1.

7.0 PROCEDURE

7.1 Semivolatile organic sample extraction: Water, soil/sediment, sludge, and waste samples requiring analysis for base/neutral and acid extractables and/or organochlorine pesticides must undergo solvent extraction prior to analysis. This manual contains four methods that may be used for this purpose: Method 3510; Method 3520; Method 3540; and Method 3550. The method that should be used on a particular sample, is highly dependent upon the physical characteristics of that sample. Therefore, review these four methods prior to choosing one in particular. Appropriate surrogate standards and, if necessary, matrix spiking solutions are added to the sample prior to extraction for all four methods.

7.1.1 Method 3510: Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is solvent extracted using a separatory funnel. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Method 3520 should be used if an emulsion forms between the solvent-sample phases, which can not be broken up by mechanical techniques.

7.1.2 Method 3520: Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is extracted with an organic solvent in a continuous liquid-liquid extractor. The solvent must have a density greater than that of the sample. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. The limitations of Method 3510 concerning solvent-sample phase separation do not interfere with this procedure.

7.1.3 Method 3540: This is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. A solid sample is mixed with anhydrous sodium sulfate, placed into an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The

extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis.

7.1.4 Method 3550: This method is applicable to the extraction of nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes using the technique of ultrasonic extraction. Two procedures are detailed depending upon the expected concentration of organics in the sample; a low concentration and a high concentration method. In both, a known weight of sample is mixed with anhydrous sodium sulfate and solvent extracted using ultrasonic extraction. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis.

7.1.5 Method 3580: This method describes the technique of solvent dilution of non-aqueous waste samples. It is designed for wastes that may contain organic chemicals at a level greater than 20,000 mg/kg and that are soluble in the dilution solvent. When using this method, the analyst must use caution in determining the correct concentration of spike and surrogate solution to avoid diluting out these compounds when diluting the sample. The loss of surrogate and spike data should only occur in samples containing a high concentration of analytes which is unknown at the time of extraction or where sample interferences could not be eliminated following the best attempts at extract cleanup by the laboratory.

7.2 Volatile organic sample preparation: There are three methods for volatile sample preparation: Method 5030; Method 5040; and direct injection. Method 5030 is the most widely applicable procedure for analysis of volatile organics, while the direct injection technique may have limited applicability to aqueous matrices.

7.2.1 Method 5030: This method describes the technique of purge-and-trap for the introduction of purgeable organics into a gas chromatograph. This procedure is applicable for use with aqueous samples directly and to solids, wastes, soils/sediments, and water-miscible liquids following appropriate preparation. An inert gas is bubbled through the sample, which will efficiently transfer the purgeable organics from the aqueous phase to the vapor phase. The vapor phase is swept through a sorbent trap where the purgeables are trapped. After purging is completed, the trap is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. Prior to application of the purge-and-trap procedure, all samples (including blanks, spikes, and duplicates) should be spiked with surrogate standards and, if required, with matrix spiking compounds.

7.2.2 Method 5040: This method is applicable to the investigation of sorbent cartridges from volatile organic sampling train (VOST).

7.3 Sample analysis: Following preparation of a sample by one of the methods described above, the sample is ready for further analysis. For samples requiring volatile organic analysis, application of one of the methods described above is followed directly by gas chromatographic analysis (Methods 8010, 8011, 8015, 8020, 8021, 8030, 8240 and 8260). Samples prepared for semivolatile analysis may, if necessary, undergo cleanup (See Method 3600) prior to application of a specific determinative method.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific guidance on quality control procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of a reagent water blank that all glassware and reagents are interference free. Each time a set of samples is processed, a method blank(s) should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.3 Surrogate standards should be added to all samples when specified in the appropriate determinative method in Chapter Four, Section 4.3

8.4 A reagent blank, a matrix spike, and a duplicate or matrix spike duplicate must be performed for each analytical batch (up to a maximum of 20 samples) analyzed.

8.5 For GC or GC/MS analysis, the analytical system performance must be verified by analyzing quality control (QC) check samples. Method 8000, Section 8.0 discusses in detail the process of verification; however, preparation of the QC check sample concentrate is dependent upon the method being evaluated.

8.5.1 **Volatile organic QC check samples:** QC check sample concentrates containing each analyte of interest are spiked into reagent water (defined as the QC check sample) and analyzed by purge-and-trap (Method 5030). The concentration of each analyte in the QC check sample is 20 µg/L. The evaluation of system performance is discussed in detail in Method 8000, beginning with Paragraph 8.6

8.5.2 **Semivolatile organic QC check samples:** To evaluate the performance of the analytical method, the QC check samples must be handled in exactly the same manner as actual samples. Therefore, 1.0 mL of the QC check sample concentrate is spiked into each of four 1-L aliquots of reagent water (now called the QC check sample), extracted, and then analyzed by GC. The variety of semivolatile analytes which may be analyzed by GC is such that the concentration of the QC check sample concentrate is different for the different analytical techniques presented in the manual. Method 8000 discusses in detail the procedure of verifying the detection system once the QC check sample has been prepared. The concentrations of the QC check sample concentrate for the various methods are as follows:

8.5.2.1 Method 8040 - Phenols: The QC check sample concentrate should contain each analyte at a concentration of 100 mg/L in 2-propanol.

8.5.2.2 Method 8060 - Phthalate esters: The QC check sample concentrate should contain the following analytes at the following concentrations in acetone: butyl benzyl phthalate, 10 mg/L; bis(2-ethylhexyl) phthalate, 50 mg/L; di-n-octylphthalate, 50 mg/L; and any other phthalate at 25 mg/L.

8.5.2.3 Method 8070 - Nitrosamines: The QC check sample concentrate should contain each analyte at 20 mg/L in methanol or some other water miscible solvent.

8.5.2.4 Method 8080 - Organochlorine pesticides and PCBs: The QC check sample concentrate should contain each single-component analyte at the following concentrations in acetone or some other water miscible solvent: 4,4'-DDD, 10 mg/L; 4,4'-DDT, 10 mg/L; endosulfan II, 10 mg/L; endosulfan sulfate, 10 mg/L; endrin, 10 mg/L; and any other single-component pesticide at 2 mg/L . If the method is only to be used to analyze PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 mg/L in acetone.

8.5.2.5 Method 8090 - Nitroaromatics and Cyclic Ketones: The QC check sample concentrate should contain each analyte at the following concentrations in acetone: each dinitrotoluene at 20 mg/L; and isophorone and nitrobenzene at 100 mg/L.

8.5.2.6 Method 8100 - Polynuclear aromatic hydrocarbons: The QC check sample concentrate should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 mg/L; acenaphthylene, 100 mg/L; acenaphthene, 100 mg/L; fluorene, 100 mg/L; phenanthrene, 100 mg/L; anthracene, 100 mg/L; benzo(k)fluoranthene, 5 mg/L; and any other PAH at 10 mg/L .

8.3.2.7 Method 8110 - Haloethers: The QC check sample concentrate should contain each analyte at a concentration of 20 mg/L in methanol or some other water miscible solvent.

8.5.2.8 Method 8120 - Chlorinated hydrocarbons: The QC check sample concentrate should contain each analyte at the following concentrations in acetone: hexachloro-substituted hydrocarbons, 10 mg/L; and any other chlorinated hydrocarbon, 100 mg/L.

8.3.2.9 Method 8140/8141 - Organophosphorus compounds: The QC check sample concentrate should contain each analyte in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

8.3.2.10 Method 8150 - Chlorinated herbicides: The QC check sample concentrate should contain each analyte in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

8.3.2.11 Method 8250/8270 - Semivolatile organics: The QC check sample concentrate should contain each analyte in acetone at a concentration of 100 mg/L.

8.3.2.12 Method 8310 - Polynuclear aromatic hydrocarbons: The QC check sample concentrate should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 mg/L;

acenaphthylene, 100 mg/L; acenaphthene, 100 mg/L; fluorene, 100 mg/L; phenanthrene, 100 mg/L; anthracene, 100 mg/L; benzo(k)fluoranthene, 5 mg/L; and any other PAH at 10 mg/L.

9.0 METHOD PERFORMANCE

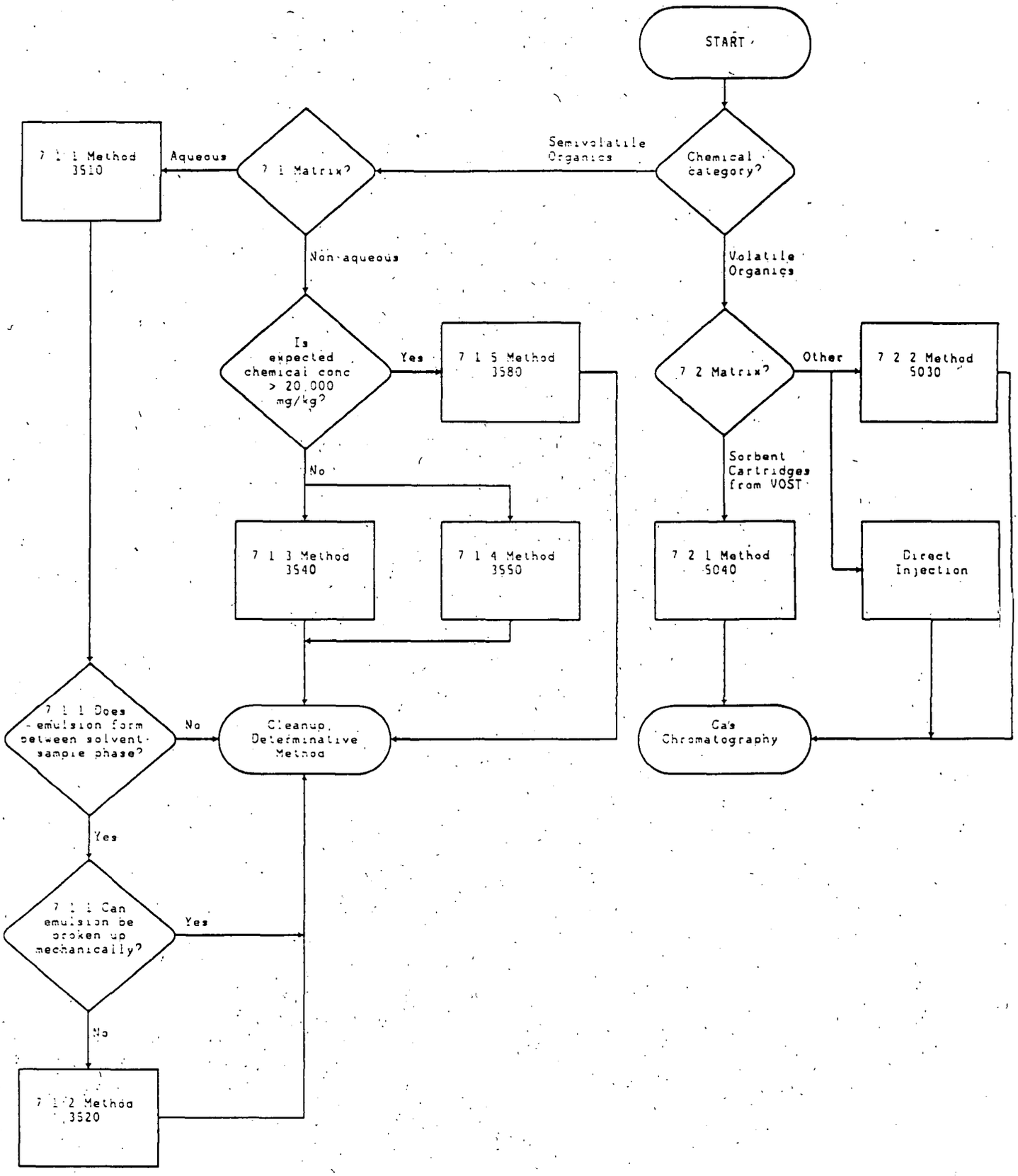
9.1 The recovery of surrogate standards is used to monitor unusual matrix effects, sample processing problems, etc. The recovery of matrix spiking compounds indicates the presence or absence of unusual matrix effects.

9.2 The performance of this method will be dictated by the overall performance of the sample preparation in combination with the analytical determinative method.

10.0 REFERENCES

10.1 None required.

METHOD 3500A
ORGANIC EXTRACTION AND SAMPLE PREPARATION



METHOD 3510A

SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative methods described in Section 4.3 of Chapter Four.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, at a specified pH (see Table 1), is serially extracted with methylene chloride using a separatory funnel. The extract is dried, concentrated (if necessary), and, as necessary, exchanged into a solvent compatible with the cleanup or determinative step to be used.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Separatory funnel - 2-liter, with Teflon stopcock.

4.2 Drying column - 20-mm i.d. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.3.3 Snyder column - Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two-ball micro (Kontes K-569001-0219 or equivalent).

4.4 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.6 Vials - Glass, 2-mL capacity with Teflon lined screw-caps or crimp tops.

4.7 pH indicator paper - pH range including the desired extraction pH.

4.8 Erlenmeyer flask - 250-mL.

4.9 Syringe - 5-mL.

4.10 Graduated cylinder - 1-liter.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium hydroxide solution (10N), NaOH. Dissolve 40 g NaOH in water and dilute to 100 mL.

5.4 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.5 Sulfuric acid solution (1:1), H_2SO_4. Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of water.

5.6 Extraction/exchange solvents (See Table 1 for choice of extraction/exchange solvents).

5.6.1 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.6.2 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.6.3 2-Propanol, $CH_3CH(OH)CH_3$ - Pesticide quality or equivalent.

5.6.4 Cyclohexane, C_6H_{12} - Pesticide quality or equivalent.

5.6.5 Acetonitrile, CH_3CN - Pesticide quality or equivalent.

5.6.6 Methanol, CH_3OH - Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Using a 1-liter graduated cylinder, measure 1 liter (nominal) of sample and transfer it to the separatory funnel. If high concentrations are anticipated, a smaller volume may be used and then diluted with water to 1 liter. Add 1.0 mL of the surrogate standards to all samples, spikes, and blanks (see Method 3500 and the determinative method to be used for details on the surrogate standard solution and the matrix spike solution). For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/µL of each base/neutral analyte and 200 ng/µL of each acid analyte in the extract to be analyzed (assuming a 1 µL injection). If Method 3640, Gel-Permeation Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.2 Check the pH of the sample with wide-range pH paper and, if necessary, adjust the pH to that indicated in Table 1 for the specific determinative method that will be used to analyze the extract.

7.3 Add 60 mL of methylene chloride to the separatory funnel.

7.4 Seal and shake the separatory funnel vigorously for 1-2 minutes with periodic venting to release excess pressure.

<u>NOTE</u>: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to prevent unnecessary exposure of the analyst to the organic vapor.

7.5 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass

wool, centrifugation, or other physical methods. Collect the solvent extract in an Erlenmeyer flask. If the emulsion cannot be broken (recovery of < 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Method 3520.

7.6 Repeat the extraction two more times using fresh portions of solvent (Sections 7.3 through 7.5). Combine the three solvent extracts.

7.7 If further pH adjustment and extraction is required, adjust the pH of the aqueous phase to the desired pH indicated in Table 1. Serially extract three times with 60 mL of methylene chloride, as outlined in Sections 7.3 through 7.5. Collect and combine the extracts and label the combined extract appropriately.

7.8 If performing GC/MS analysis (Method 8250 or 8270), the acid and base/neutral extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid and base/neutral extracts may be preferable (e.g. if for regulatory purposes the presence or absence of specific acid or base/neutral compounds at low concentrations must be determined, separate extract analyses may be warranted).

7.9 Assemble a Kuderna-Danish (K-D) concentrator (if necessary) by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.10 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the Erlenmeyer flask, which contained the solvent extract, with 20-30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

7.11 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.12 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent, a new boiling chip, and reattach the Snyder column. Concentrate the extract, as described in Section 7.11, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.13 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent.

If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Section 7.14 or adjusted to 10.0 mL with the solvent last used.

7.14 If further concentration is indicated in Table 1, add another clean boiling chip to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 0.2 mL of extraction solvent. Adjust the final volume to 1.0-2.0 mL, as indicated in Table 1, with solvent.

7.15 The extract obtained (from either Section 7.13 or 7.14) may now be analyzed for analyte content using a variety of organic techniques. If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days, it should be transferred to a vial with a Teflon lined screw-cap, and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

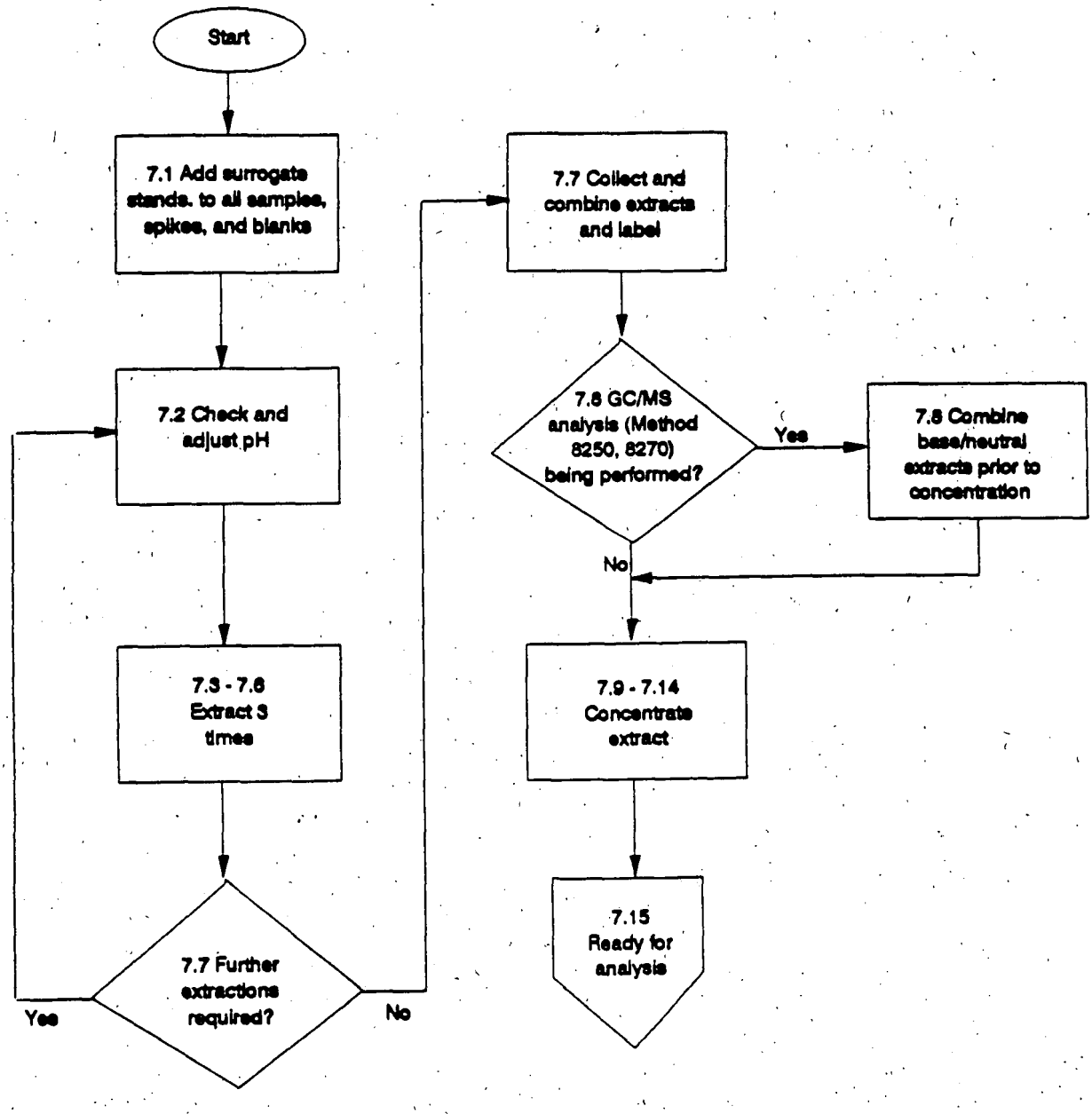
2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, D.C., 1986.

TABLE 1.
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040	≤2	none	2-propanol	hexane	1.0	1.0, 10.0[a]
8060	as received	none	hexane	hexane	2.0	10.0
8070	as received	none	methanol	methylene chloride	2.0	10.0
8080	5-9	none	hexane	hexane	10.0	10.0
8090	5-9	none	hexane	hexane	2.0	1.0
8100	as received	none	none	cyclohexane	2.0	1.0
8110	as received	none	hexane	hexane	2.0	10.0
8120	as received	none	hexane	hexane	2.0	1.0
8140	6-8	none	hexane	hexane	10.0	10.0
8141	as received	none	hexane	hexane	10.0	10.0
8250[b]	>11	<2	none	-	-	1.0
8270[b]	>11	<2	none	-	-	1.0
8310	as received	none	acetonitrile	-	-	1.0

a Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

b The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.


Start
7.1 Add surrogate stands. to all samples, spikes, and blanks
7.2 Check and adjust pH
7.3 - 7.6 Extract 3 times
7.7 Further extractions required?
Yes
No
7.7 Collect and combine extracts and label
7.8 GC/MS analysis (Method 8250, 8270) being performed?
Yes
No
7.8 Combine base/neutral extracts prior to concentration
7.9 - 7.14 Concentrate extract
7.15 Ready for analysis

METHOD 3510B

SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative methods described in Sec. 4.3 of Chapter Four.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, at a specified pH (see Table 1), is serially extracted with methylene chloride using a separatory funnel. The extract is dried, concentrated (if necessary), and, as necessary, exchanged into a solvent compatible with the cleanup or determinative method to be used (see Table 1 for appropriate exchange solvents).

3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 Under basic extraction conditions required to separate analytes for the packed columns of Method 8250, the decomposition of some analytes has been demonstrated. Organochlorine pesticides may dechlorinate, phthalate esters may exchange, and phenols may react to form tannates. These reactions increase with increasing pH, and are decreased by the shorter reaction times available in Method 3510. Methods 3520/8270, 3510/8270, and 3510/8250, respectively, are preferred over Method 3520/8250 for the analysis of these classes of compounds.

4.0 APPARATUS AND MATERIALS

4.1 Separatory funnel - 2 liter, with Teflon stopcock.

4.2 Drying column - 20 mm ID Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus.

4.3.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.4 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.6 Vials - 2 mL, glass with Teflon lined screw-caps or crimp tops.

4.7 pH indicator paper - pH range including the desired extraction pH.

4.8 Erlenmeyer flask - 250 mL.

4.9 Syringe - 5 mL.

4.10 Graduated cylinder - 1 liter.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium hydroxide solution (10N), NaOH. Dissolve 40 g NaOH in organic-free reagent water and dilute to 100 mL.

5.4 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with

methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.5 Sulfuric acid solution (1:1 v/v), H_2SO_4. Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of organic-free reagent water.

5.6 Extraction/exchange solvents

5.6.1 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.6.2 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.6.3 2-Propanol, $CH_3CH(OH)CH_3$ - Pesticide quality or equivalent.

5.6.4 Cyclohexane, C_6H_{12} - Pesticide quality or equivalent.

5.6.5 Acetonitrile, CH_3CN - Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Using a 1 liter graduated cylinder, measure 1 liter (nominal) of sample and transfer it quantitatively to the separatory funnel. If high concentrations are anticipated, a smaller volume may be used and then diluted with organic-free reagent water to 1 liter. Add 1.0 mL of the surrogate standards to all samples, spikes, and blanks (see Method 3500 and the determinative method to be used, for details on the surrogate standard solution and the matrix spike solution). For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/μL of each base/neutral analyte and 200 ng/μL of each acid analyte in the extract to be analyzed (assuming a 1 μL injection). If Method 3640, Gel-Permeation Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.2 Check the pH of the sample with wide-range pH paper and, if necessary, adjust the pH to that indicated in Table 1 for the specific determinative method that will be used to analyze the extract.

7.3 Add 60 mL of methylene chloride to the separatory funnel.

7.4 Seal and shake the separatory funnel vigorously for 1-2 minutes with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. Venting of the separatory funnel should be into a hood to avoid needless exposure of the analyst to solvent vapors.

7.5 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the solvent extract in an Erlenmeyer flask. If the emulsion cannot be broken (recovery of < 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Method 3520, Continuous Liquid-Liquid Extraction.

7.6 Repeat the extraction two more times using fresh portions of solvent (Secs. 7.3 through 7.5). Combine the three solvent extracts.

7.7 If further pH adjustment and extraction is required, adjust the pH of the aqueous phase to the desired pH indicated in Table 1. Serially extract three times with 60 mL of methylene chloride, as outlined in Secs. 7.3 through 7.5. Collect and combine the extracts and label the combined extract appropriately.

7.8 If performing GC/MS analysis (Method 8270), the acid/neutral and base extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid/neutral and base extracts may be preferable (e.g. if for regulatory purposes the presence or absence of specific acid/neutral or base compounds at low concentrations must be determined, separate extract analyses may be warranted).

7.9 Perform the concentration (if necessary) using the Kuderna-Danish (K-D) Technique (Secs. 7.10.1 through 7.10.4).

7.10 K-D Technique

7.10.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporation flask. Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the Erlenmeyer flask, which contained the solvent extract, with 20-30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

7.10.2 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot

vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.10.3 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent, a new boiling chip, and reattach the Snyder column. Concentrate the extract, as described in Sec. 7.11, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.10.4 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Sec. 7.11 or adjusted to 10.0 mL with the solvent last used.

7.11 If further concentration is indicated in Table 1, either the micro-Snyder column technique (7.11.1) or nitrogen blowdown technique (7.11.2) is used to adjust the extract to the final volume required.

7.11.1 Micro-Snyder Column Technique

7.11.1.1 If further concentration is indicated in Table 1, add another clean boiling chip to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 0.2 mL of extraction solvent. Adjust the final volume to 1.0-2.0 mL, as indicated in Table 1, with solvent.

7.11.2 Nitrogen Blowdown Technique

7.11.2.1 Place the concentrator tube in a warm bath (35°C) and evaporate the solvent volume to 0.5 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

<u>CAUTION</u>: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce interferences.

7.11.2.2 The internal wall of the tube must be rinsed down several times with methylene chloride or appropriate solvent during the operation. During evaporation, the tube solvent level must be positioned to avoid water condensation. Under normal procedures, the extract must not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 ml, semivolatile analytes may be lost.

7.12 The extract may now be analyzed for the target analytes using the appropriate determinative technique(s) (see Sec. 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days it should be transferred to a vial with a Teflon lined screw-cap or crimp top, and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

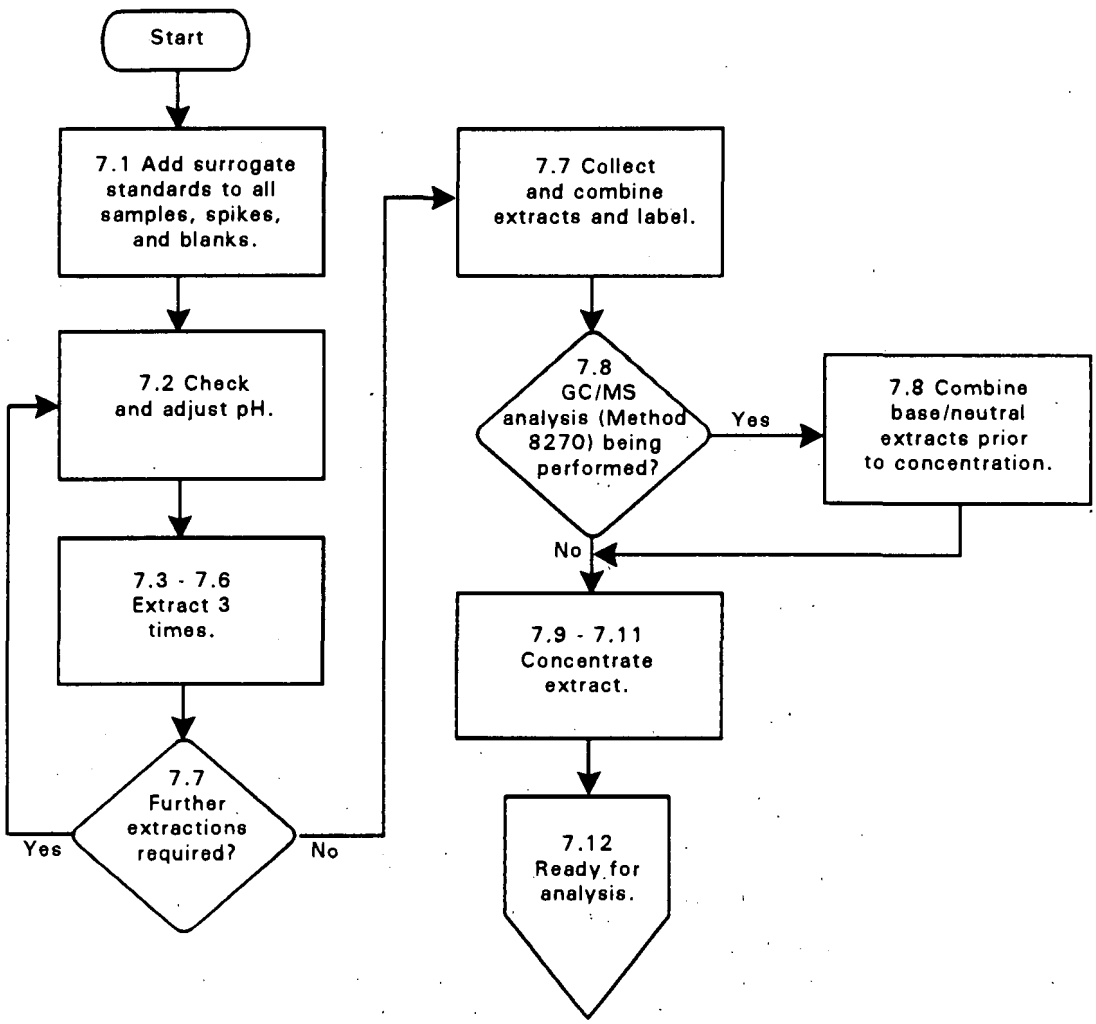
10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

TABLE 1.
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040	≤2	none	2-propanol	hexane	1.0	1.0, 10.0[a]
8060	as received	none	hexane	hexane	2.0	10.0
8061	as received	none	hexane	hexane	2.0	10.0
8070	as received	none	methanol	methylene chloride	2.0	10.0
8080	5-9	none	hexane	hexane	10.0	10.0
8081	5-9	none	hexane	hexane	10.0	10.0
8090	5-9	none	hexane	hexane	2.0	1.0
8100	as received	none	none	cyclohexane	2.0	1.0
8110	as received	none	hexane	hexane	2.0	10.0
8120	as received	none	hexane	hexane	2.0	1.0
8121	as received	none	hexane	hexane	2.0	1.0
8140	6-8	none	hexane	hexane	10.0	10.0
8141	as received	none	hexane	hexane	10.0	10.0
8250[bc]	>11	<2	none	-	-	1.0
8270[bd]	<2	>11	none	-	-	1.0
8310	as received	none	acetonitrile	-	-	1.0
8321	as received	none	methanol	-	-	1.0
8410	as received	none	methylene chloride	methylene chloride	10.0	0.0 (dry)

a Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.
b The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.
c Loss of phthalate esters, organochlorine pesticides and phenols can occur under these extraction conditions (see Sec. 3.2).
d Extraction pH sequence may be reversed to better separate acid and neutral waste components. Excessive pH adjustments may result in the loss of some analytes (see Sec. 3.2).


Start
7.1 Add surrogate standards to all samples, spikes, and blanks.
7.2 Check and adjust pH.
7.3 - 7.6 Extract 3 times.
7.7 Further extractions required?
Yes
No
7.7 Collect and combine extracts and label.
7.8 GC/MS analysis (Method 8270) being performed?
Yes
7.8 Combine base/neutral extracts prior to concentration.
No
7.9 - 7.11 Concentrate extract.
7.12 Ready for analysis.

METHOD 3520A

CONTINUOUS LIQUID-LIQUID EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative steps described in Section 4.3 of Chapter Four.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly soluble organics in preparation for a variety of chromatographic procedures.

1.3 Method 3520 is designed for extraction solvents with greater density than the sample. Continuous extraction devices are available for extraction solvents that are less dense than the sample. The analyst must demonstrate the effectiveness of any such automatic extraction device before employing it in sample extraction.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, is placed into a continuous liquid-liquid extractor, adjusted, if necessary, to a specific pH (see Table 1), and extracted with organic solvent for 18-24 hours. The extract is dried, concentrated (if necessary), and, as necessary, exchanged into a solvent compatible with the determinative step being employed.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Continuous liquid-liquid extractor - Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf Extractor -- Ace Glass Company, Vineland, New Jersey, P/N 6841-10, or equivalent).

4.2 Drying column - 20 mm i.d. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.4 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.6 Vials - 2-mL, glass with Teflon lined screw-caps or crimp tops.

4.7 pH indicator paper - pH range including the desired extraction pH.

4.8 Heating mantle - Rheostat controlled.

4.9 Syringe - 5-mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium hydroxide solution (10N), NaOH. Dissolve 40 g NaOH in water and dilute to 100 mL.

5.4 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.5 Sulfuric acid solution (1:1), H_2SO_4. Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of water.

5.6 Extraction/exchange solvents (See Table 1 for choice of extraction/exchange solvents).

5.6.1 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.6.2 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.6.3 2-Propanol, $(CH_3)_2CHOH$ - Pesticide quality or equivalent.

5.6.4 Cyclohexane, C_6H_{12} - Pesticide quality or equivalent.

5.6.5 Acetonitrile, CH_3CN - Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Using a graduated cylinder, measure out 1 liter (nominal) of sample and transfer it to the continuous extractor. If high concentrations are anticipated, a smaller volume may be used and then diluted with water to 1 liter. Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to the pH indicated in Table 1. Pipet 1.0 mL of the surrogate standard spiking solution into each sample into the extractor and mix well. (See Method 3500 and the determinative method to be used for details on the surrogate standard solution and the matrix spike solution.) For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount of the surrogates and matrix spiking compounds added to the sample should result in a final concentration of 100 ng/μL of each base/neutral analyte and 200 ng/μL of each acid analyte in the extract to be analyzed (assuming a 1 μL injection). If Method 3640, Gel-Permeation Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.2 Add 300-500 mL of methylene chloride to the distilling flask. Add several boiling chips to the flask.

7.3 Add sufficient water to the extractor to ensure proper operation and extract for 18-24 hours.

7.4 Allow to cool; then detach the boiling flask. If extraction at a secondary pH is not required (see Table 1), the extract is dried and concentrated as described in Sections 7.7 through 7.11.

7.5 Carefully, while stirring, adjust the pH of the aqueous phase to <2 with sulfuric acid (1:1). Attach a clean distilling flask containing 500 mL of methylene chloride to the continuous extractor. Extract for 18-24 hours, allow to cool, and detach the distilling flask.

7.6 If performing GC/MS analysis (Method 8250 or 8270), the acid and base/neutral extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid and base/neutral extracts may be preferable (e.g. if for regulatory purposes the presence or absence of specific acid or base/neutral compounds at low concentrations must be determined, separate extract analyses may be warranted).

7.7 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.8 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the flask which contained the solvent extract with 20-30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

7.9 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of extraction solvent.

7.10 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent, a new boiling chip, and reattach the Snyder column. Concentrate the extract, as described in Section 7.9, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.11 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Section 7.12 or adjusted to 10.0 mL with the solvent last used.

7.12 Add another one or two clean boiling chips to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter,

but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column, rinse the flask and its lower joints into the concentrator tube with 0.2 mL of methylene chloride or exchange solvent, and adjust the final volume to 1.0 to 2.0 mL, as indicated in Table 1, with solvent.

7.13 The extracts obtained may now be analyzed for analyte content using a variety of organic techniques (see Section 4.3 of this chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days it should be transferred to a vial with a Teflon lined screw-cap and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks, matrix spike, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample-preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

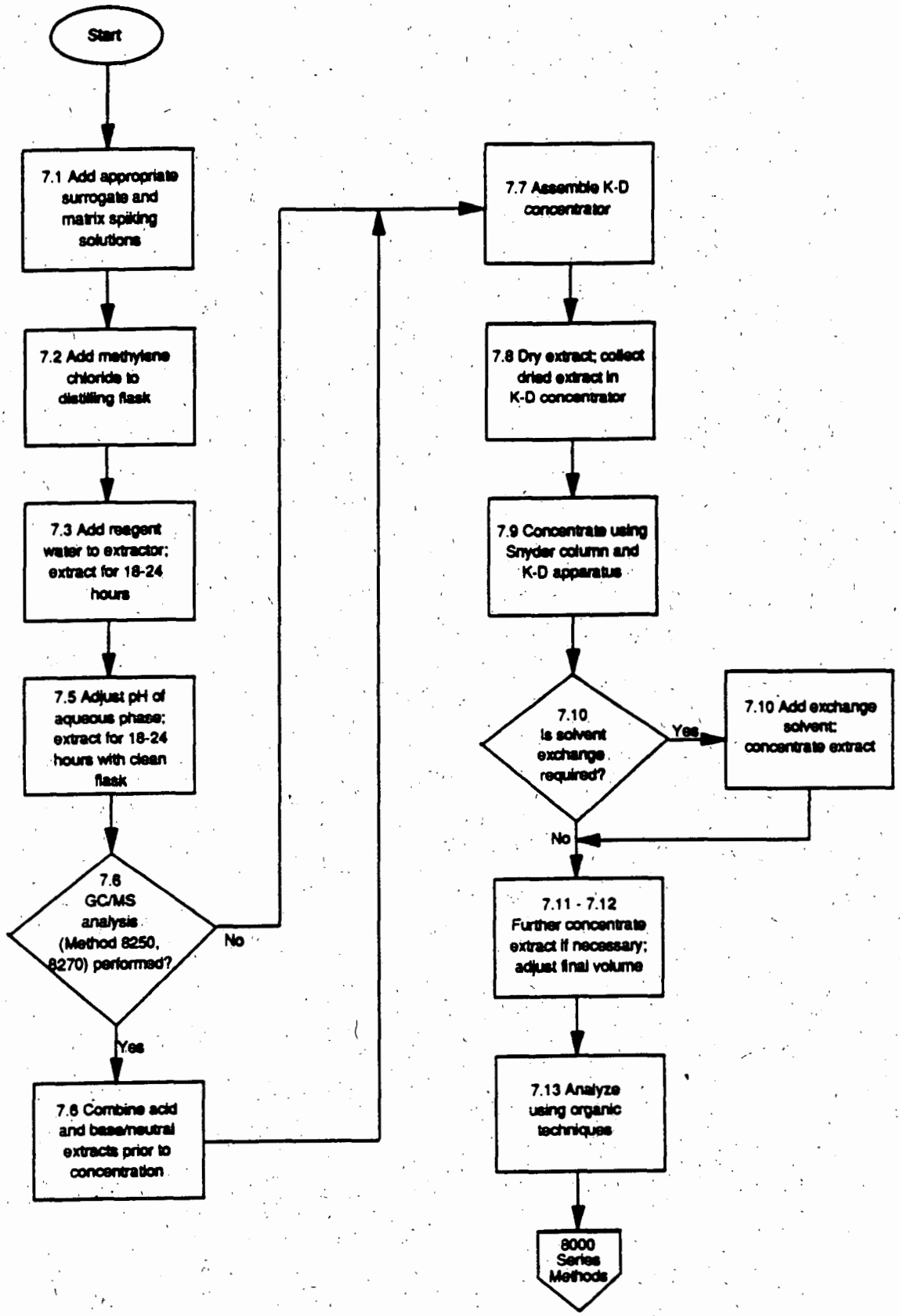
2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, D.C., 1986

TABLE 1.
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040	≤2	none	2-propanol	hexane	1.0	1.0,10.0[a]
8060	as received	none	hexane	hexane	2.0	10.0
8070	as received	none	methanol	methylene chloride	2.0	10.0
8080	5-9	none	hexane	hexane	10.0	10.0
8090	5-9	none	hexane	hexane	2.0	1.0
8100	as received	none	none	cyclohexane	2.0	1.0
8110	as received	none	hexane	hexane	2.0	10.0
8120	as received	none	hexane	hexane	2.0	1.0
8140	6-8	none	hexane	hexane	10.0	10.0
8141	as received	none	hexane	hexane	10.0	10.0
8250[b]	>11	<2	none	-	-	1.0
8270[b]	>11	<2	none	-	-	1.0
8310	as received	none	acetonitrile	-	-	1.0

a Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

b The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.


Start
7.1 Add appropriate surrogate and matrix spiking solutions
7.2 Add methylene chloride to distilling flask
7.3 Add reagent water to extractor; extract for 18-24 hours
7.5 Adjust pH of aqueous phase; extract for 18-24 hours with clean flask
7.6 GC/MS analysis (Method 8250, 8270) performed?
No
Yes
7.8 Combine acid and base/neutral extracts prior to concentration
7.7 Assemble K-D concentrator
7.8 Dry extract; collect dried extract in K-D concentrator
7.9 Concentrate using Snyder column and K-D apparatus
7.10 Is solvent exchange required?
Yes
7.10 Add exchange solvent; concentrate extract
No
7.11 - 7.12 Further concentrate extract if necessary; adjust final volume
7.13 Analyze using organic techniques
8000 Series Methods

3520B

METHOD 3520B

CONTINUOUS LIQUID-LIQUID EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative steps described in Sec. 4.3 of Chapter Four.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly soluble organics in preparation for a variety of chromatographic procedures.

1.3 Method 3520 is designed for extraction solvents with greater density than the sample. Continuous extraction devices are available for extraction solvents that are less dense than the sample. The analyst must demonstrate the effectiveness of any such automatic extraction device before employing it in sample extraction.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, is placed into a continuous liquid-liquid extractor, adjusted, if necessary, to a specific pH (see Table 1), and extracted with organic solvent for 18-24 hours. The extract is dried, concentrated (if necessary), and, as necessary, exchanged into a solvent compatible with the cleanup or determinative method being employed (see Table 1 for appropriate exchange solvents).

3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 Under basic extraction conditions required to separate analytes for the packed columns of Method 8250, the decomposition of some analytes has been demonstrated. Organochlorine pesticides may dechlorinate, phthalate esters may exchange, and phenols may react to form tannates. These reactions increase with increasing pH, and are decreased by the shorter reaction times available in Method 3510. Methods 3520/8270, 3510/8270, and 3510/8250, respectively, are preferred over Method 3520/8250 for the analysis of these classes of compounds.

4.0 APPARATUS AND MATERIALS

4.1 Continuous liquid-liquid extractor - Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Kontes 584200-0000, 584500-0000, 583250-0000, or equivalent).

4.2 Drying column - 20 mm ID Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.4 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.6 Vials - 2 mL, glass with Teflon lined screw-caps or crimp tops.

4.7 pH indicator paper - pH range including the desired extraction pH.

4.8 Heating mantle - Rheostat controlled.

4.9 Syringe - 5 mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium hydroxide solution (10N), NaOH. Dissolve 40 g NaOH in organic-free reagent water and dilute to 100 mL.

5.4 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.5 Sulfuric acid solution (1:1 v/v), H_2SO_4. Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of organic-free reagent water.

5.6 Extraction/exchange solvents

5.6.1 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.6.2 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.6.3 2-Propanol, $(CH_3)_2CHOH$ - Pesticide quality or equivalent.

5.6.4 Cyclohexane, C_6H_{12} - Pesticide quality or equivalent.

5.6.5 Acetonitrile, CH_3CN - Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Using a 1 liter graduated cylinder, measure out 1 liter (nominal) of sample and transfer it quantitatively to the continuous extractor. If high concentrations are anticipated, a smaller volume may be used and then diluted with organic-free reagent water to 1 liter. Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to the pH indicated in Table 1 using 1:1 (V/V) sulfuric acid or 10 N sodium hydroxide. Pipet 1.0 mL of the surrogate standard spiking solution into each sample into the extractor and mix well. (See Method 3500 and the determinative method to be used, for details on the surrogate standard solution and the matrix spike solution.) For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount of the surrogates and matrix spiking compounds added to the sample should result in a final concentration of 100 ng/μL of each base/neutral analyte and 200 ng/μL of each acid analyte in the extract to be analyzed (assuming a 1 μL injection). If Method 3640, Gel-Permeation Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.2 Add 300-500 mL of methylene chloride to the distilling flask. Add several boiling chips to the flask.

7.3 Add sufficient water to the extractor to ensure proper operation and extract for 18-24 hours.

7.4 Allow to cool; then detach the boiling flask. If extraction at a secondary pH is not required (see Table 1), the extract is dried and concentrated using one of the techniques referred to in Sec. 7.7.

7.5 Carefully, while stirring, adjust the pH of the aqueous phase to the second pH indicated in Table 1. Attach a clean distilling flask containing 500 mL of methylene chloride to the continuous extractor. Extract for 18-24 hours, allow to cool, and detach the distilling flask.

7.6 If performing GC/MS analysis (Method 8270), the acid/neutral and base extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid/neutral and base extracts may be preferable (e.g. if for regulatory purposes the presence or absence of specific acid/neutral and base compounds at low concentrations must be determined, separate extract analyses may be warranted).

7.7 Perform concentration (if necessary) using the Kuderna-Danish (K-D) Technique (Secs. 7.8.1 through 7.8.4).

7.8 K-D Technique

7.8.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporation flask. Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the flask which contained the solvent extract with 20-30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

7.8.2 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of extraction solvent.

7.8.3 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent, a new boiling chip, and reattach the Snyder column. Concentrate the extract, as described in Sec. 7.9, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.8.4 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the techniques outlined in Sec. 7.9 or adjusted to 10.0 mL with the solvent last used.

7.9 If further concentration is indicated in Table 1, either the micro-Snyder column technique (7.9.1) or nitrogen blowdown technique (7.9.2) is used to adjust the extract to the final volume required.

7.9.1 Micro-Snyder Column Technique

7.9.1.1 Add another one or two clean boiling chips to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column, rinse the flask and its lower joints into the concentrator tube with 0.2 mL of methylene chloride or exchange solvent, and adjust the final volume to 1.0 to 2.0 mL, as indicated in Table 1, with solvent.

7.9.2 Nitrogen Blowdown Technique

7.9.2.1 Place the concentrator tube in a warm bath (35°C) and evaporate the solvent volume to 0.5 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

<u>CAUTION</u>: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce interferences.

7.9.2.2 The internal wall of the tube must be rinsed down several times with methylene chloride or appropriate solvent during the operation. During evaporation, the tube solvent level must be positioned to avoid water condensation. Under normal procedures, the extract must not be allowed to become dry.

<u>CAUTION</u>: When the volume of solvent is reduced below 1 ml, semivolatile analytes may be lost.

7.10 The extract may now be analyzed for the target analytes using the appropriate determinative technique(s) (see Sec. 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer

than 2 days it should be transferred to a vial with a Teflon lined screw-cap or crimp top, and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks, matrix spike, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample-preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

TABLE 1.
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

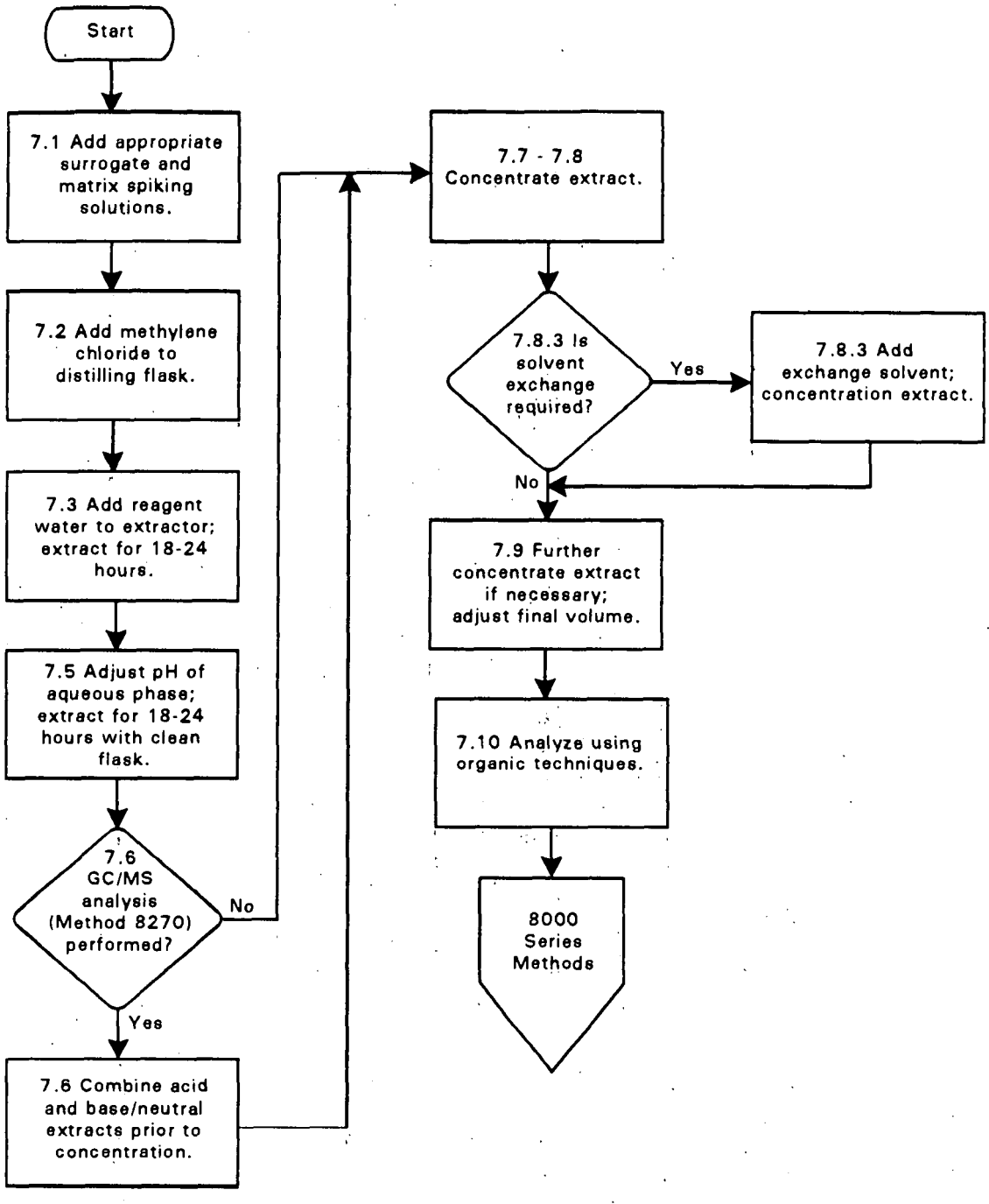
Determinative method	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040	≤2	none	2-propanol	hexane	1.0	1.0,10.0[a]
8060	as received	none	hexane	hexane	2.0	10.0
8061	as received	none	hexane	hexane	2.0	10.0
8070	as received	none	methanol	methylene chloride	2.0	10.0
8080	5-9	none	hexane	hexane	10.0	10.0
8081	5-9	none	hexane	hexane	10.0	10.0
8090	5-9	none	hexane	hexane	2.0	1.0
8100	as received	none	none	cyclohexane	2.0	1.0
8110	as received	none	hexane	hexane	2.0	10.0
8120	as received	none	hexane	hexane	2.0	1.0
8121	as received	none	hexane	hexane	2.0	1.0
8140	6-8	none	hexane	hexane	10.0	10.0
8141	as received	none	hexane	hexane	10.0	10.0
8250[b,c]	>11	<2	none	-	-	1.0
8270[b,d]	<2	>11	none	-	-	1.0
8310	as received	none	acetonitrile	-	-	1.0
8321	as received	none	methanol	-	-	1.0
8410	as received	none	methylene chloride	methylene chloride	10.0	0.0 (dry)

a Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

b The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

c Loss of phthalate esters, organochlorine pesticides and phenols can occur under these extraction conditions (see Sec. 3.2).

d If further separation of major acid and neutral components is required, Method 3650, Acid-Base Partition Cleanup, is recommended. Reversal of the Method 8270 pH sequence is not recommended as analyte losses are more severe under the base first continuous extraction (see Sec. 3.2).


Start
7.1 Add appropriate surrogate and matrix spiking solutions.
7.2 Add methylene chloride to distilling flask.
7.3 Add reagent water to extractor; extract for 18-24 hours.
7.5 Adjust pH of aqueous phase; extract for 18-24 hours with clean flask.
7.6 GC/MS analysis (Method 8270) performed?
No
Yes
7.6 Combine acid and base/neutral extracts prior to concentration.
7.7 - 7.8 Concentrate extract.
7.8.3 Is solvent exchange required?
Yes
7.8.3 Add exchange solvent; concentration extract.
No
7.9 Further concentrate extract if necessary; adjust final volume.
7.10 Analyze using organic techniques.
8000 Series Methods

3540A

METHOD 3540A

SOXHLET EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 Method 3540 is a procedure for extracting nonvolatile and semi-volatile organic compounds from solids such as soils, sludges, and wastes. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

2.0 SUMMARY OF METHOD

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is then dried, concentrated (if necessary), and, as necessary, exchanged into a solvent compatible with the cleanup or determinative step being employed.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extractor - 40-mm i.d., with 500-mL round-bottom flask.

4.2 Drying column - 20-mm i.d. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.4 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.6 Vials - Glass, 2-mL capacity, with Teflon lined screw-caps or crimp tops.

4.7 Glass or paper thimble or glass wool - Contaminant free.

4.8 Heating mantle - Rheostat controlled.

4.9 Syringe - 5-mL.

4.10 Apparatus for determining percent moisture

4.10.1 Oven - Drying.

4.10.2 Desiccator.

4.10.3 Crucibles - Porcelain.

4.11 Apparatus for grinding - If the sample will not pass through a 1-mm standard sieve or cannot be extruded through a 1-mm opening, it should be processed into a homogeneous sample that meets these requirements. Fisher Mortar Model 155 Grinder, Fisher Scientific Co., Catalogue Number 8-323, or an equivalent brand and model, is recommended for sample processing. This grinder should handle most solid samples, except gummy, fibrous, or oily materials.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with

methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Extraction solvents

5.4.1 Soil/sediment and aqueous sludge samples shall be extracted using either of the following solvent systems:

5.4.1.1 Toluene/Methanol ((10:1) (v/v)), $C_6H_5CH_3/CH_3OH$. Pesticide quality or equivalent.

5.4.1.2 Acetone/Hexane ((1:1) (v/v)), $CH_3COCH_3/CH_3(CH_2)_4CH_3$. Pesticide quality or equivalent.

5.4.2 Other samples shall be extracted using the following:

5.4.2.1 Methylene chloride, CH_2Cl_2. Pesticide quality or equivalent.

5.5 Exchange solvents

5.5.1 Hexane, C_6H_{14}. Pesticide quality or equivalent.

5.5.2 2-Propanol, $(CH_3)_2CHOH$. Pesticide quality or equivalent.

5.5.3 Cyclohexane, C_6H_{12}. Pesticide quality or equivalent.

5.5.4 Acetonitrile, CH_3CN. Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Sample Handling

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.2 Waste samples - Samples consisting of multiphases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.1.3 Dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.2 Determination of percent moisture - In certain cases, sample results are desired based on dry-weight basis. When such data is desired, a portion of sample for moisture determination should be weighed out at the same time as the portion used for analytical determination.

7.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\% \text{ moisture} = \frac{\text{g of sample} - \text{g of dry sample}}{\text{g of sample}} \times 100$$

7.3 Blend 10 g of the solid sample with 10 g of anhydrous sodium sulfate and place in an extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble. Add 1.0 mL of the surrogate standard spiking solution onto the sample (see Method 3500 and the determinative method to be used for details on the surrogate standard and matrix spiking solutions). For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/µL of each base/neutral analyte and 200 ng/µL of each acid analyte in the extract to be analyzed (assuming a 1 µL injection). If Method 3640, Gel-permeation cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.4 Place approximately 300 mL of the extraction solvent (Section 5.3) into a 500-mL round-bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hours at 4-6 cycles/hr.

7.5 Allow the extract to cool after the extraction is complete.

7.6 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.7 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Wash the extractor flask and sodium sulfate column with 100 to 125 mL of extraction solvent to complete the quantitative transfer.

7.8 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 minutes. At the proper rate of distillation the balls of the column

will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.9 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip, and reattach the Snyder column. Concentrate the extract as described in Section 7.6, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.10 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Section 7.9 or adjusted to 10.0 mL with the solvent last used.

7.11 If further concentration is indicated in Table 1, add another one or two clean boiling chips to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 0.2 mL of solvent. Adjust the final volume to 1.0-2.0 mL, as indicated in Table 1, with solvent.

7.12 The extracts obtained may now be analyzed for analyte content using a variety of organic techniques (see Section 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days, it should be transferred to a vial with a Teflon lined screw-cap and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, D.C., 1986.

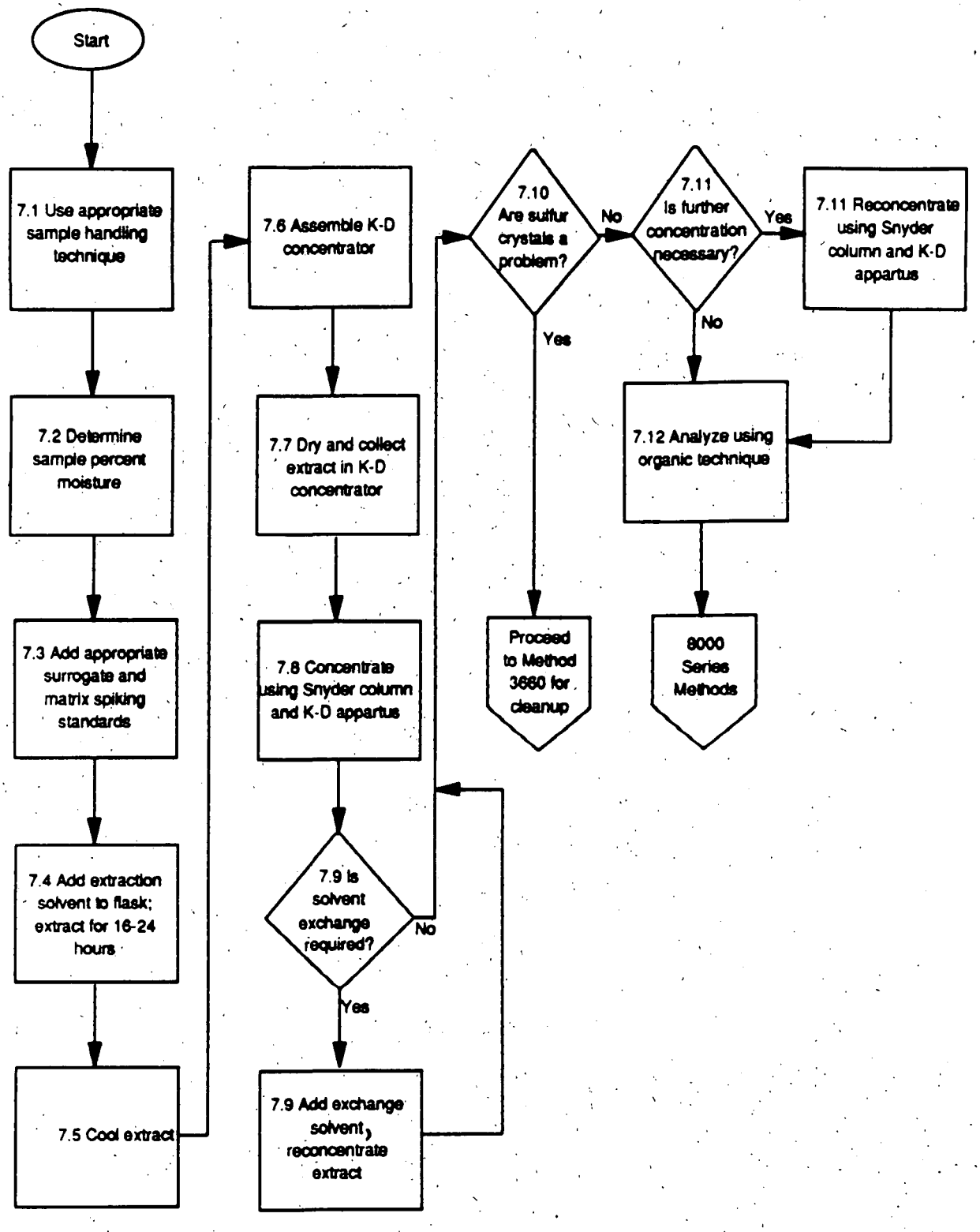
TABLE 1.
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040[a]	as received	2-propanol	hexane	1.0	1.0, 10.0[b]
8060	as received	hexane	hexane	2.0	10.0
8070	as received	methanol	methylene chloride	2.0	10.0
8080	as received	hexane	hexane	10.0	10.0
8090	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8110	as received	hexane	hexane	2.0	10.0
8120	as received	hexane	hexane	2.0	1.0
8140	as received	hexane	hexane	10.0	10.0
8141	as received	hexane	hexane	10.0	10.0
8250[a,c]	as received	none	--	--	1.0
8270[a,c]	as received	none	--	--	1.0
8310	as received	acetonitrile	--	--	1.0

[a] To obtain separate acid and base/neutral extracts, Method 3650 should be performed following concentration of the extract to 10.0 mL.

[b] Phenols may be analyzed by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optical derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

[c] The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.


Start
7.1 Use appropriate sample handling technique
7.2 Determine sample percent moisture
7.3 Add appropriate surrogate and matrix spiking standards
7.4 Add extraction solvent to flask; extract for 16-24 hours
7.5 Cool extract
7.6 Assemble K-D concentrator
7.7 Dry and collect extract in K-D concentrator
7.8 Concentrate using Snyder column and K-D appartus
7.9 Is solvent exchange required?
No
Yes
7.9 Add exchange solvent, reconcentrate extract
7.10 Are sulfur crystals a problem?
No
Yes
Proceed to Method 3660 for cleanup
7.11 Is further concentration necessary?
Yes
No
7.11 Reconcentrate using Snyder column and K-D appartus
7.12 Analyze using organic technique
8000 Series Methods

3540B

METHOD 3540B

SOXHLET EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 Method 3540 is a procedure for extracting nonvolatile and semi-volatile organic compounds from solids such as soils, sludges, and wastes. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 This method is applicable to the isolation and concentration of water insoluble and slightly water soluble organics in preparation for a variety of chromatographic procedures.

2.0 SUMMARY OF METHOD

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is then dried, concentrated (if necessary), and, as necessary, exchanged into a solvent compatible with the cleanup or determinative step being employed.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extractor - 40 mm ID, with 500 mL round bottom flask.

4.2 Drying column - 20 mm ID Pyrex chromatographic column with Pyrex glass wool at bottom.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.4 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.6 Vials - Glass, 2 mL capacity, with Teflon lined screw or crimp top.

4.7 Glass or paper thimble or glass wool - Contaminant free.

4.8 Heating mantle - Rheostat controlled.

4.9 Disposable glass pasteur pipet and bulb.

4.10 Apparatus for determining percent dry weight.

4.10.1 Oven - Drying.

4.10.2 Desiccator.

4.10.3 Crucibles - Porcelain or disposable aluminum.

4.11 Apparatus for grinding

4.12 Analytical balance - 0.0001 g.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Extraction solvents

5.4.1 Soil/sediment and aqueous sludge samples shall be extracted using either of the following solvent systems:

5.4.1.1 Acetone/Hexane (1:1) (v/v), CH_3COCH_3/C_6H_{14}. Pesticide quality or equivalent.

NOTE: This solvent system has lower disposal cost and lower toxicity.

5.4.1.2 Methylene chloride/Acetone (1:1 v/v), CH_2Cl_2/CH_3COCH_3. Pesticide quality or equivalent.

5.4.2 Other samples shall be extracted using the following:

5.4.2.1 Methylene chloride, CH_2Cl_2. Pesticide quality or equivalent.

5.4.2.2 Toluene/Methanol (10:1) (v/v), $C_6H_5CH_3/CH_3OH$. Pesticide quality or equivalent.

5.5 Exchange solvents

5.5.1 Hexane, C_6H_{14}. Pesticide quality or equivalent.

5.5.2 2-Propanol, $(CH_3)_2CHOH$. Pesticide quality or equivalent.

5.5.3 Cyclohexane, C_6H_{12}. Pesticide quality or equivalent.

5.5.4 Acetonitrile, CH_3CN. Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analysis, Sec. 4.1.

7.0 PROCEDURE

7.1 Sample Handling

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.2 Waste samples - Samples consisting of multiphases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.1.3 Dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1 mm sieve or can

be extruded through a 1 mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.1.4 Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise broken up to allow mixing, and maximum exposure of the sample surfaces for extraction. The professional judgment of the analyst is required for handling these difficult matrices.

7.2 Determination of sample % dry weight - In certain cases, sample results are desired based on dry weight basis. When such data are desired, a portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

However, samples known or suspected to contain significant concentrations of toxic, flammable, or explosive constituents should not be oven dried because of concerns for personal safety. Laboratory discretion is advised. It may be prudent to delay oven drying of the weighed-out portion until other analytical results are available.

7.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.3 Blend 10 g of the solid sample with 10 g of anhydrous sodium sulfate and place in an extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble. Add 1.0 mL of the surrogate standard spiking solution onto the sample (see Method 3500 for details on the surrogate standard and matrix spiking solutions). For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/μL of each base/neutral analyte and 200 ng/μL of each acid analyte in the extract to be analyzed (assuming a 1 μL injection). If Method 3640, Gel Permeation Chromatography Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.4 Place approximately 300 mL of the extraction solvent (Sec. 5.4) into a 500 mL round bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hours at 4-6 cycles/hr.

7.5 Allow the extract to cool after the extraction is complete.

7.6 Assemble a Kuderna-Danish (K-D) concentrator (if necessary) by attaching a 10 mL concentrator tube to a 500 mL evaporation flask.

7.7 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Wash the extractor flask and sodium sulfate column with 100 to 125 mL of extraction solvent to complete the quantitative transfer.

7.8 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.9 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add approximately 50 mL of the exchange solvent and a new boiling chip, and reattach the Snyder column. Concentrate the extract as described in Sec. 7.8, raising the temperature of the water bath, if necessary, to maintain proper distillation. When the apparent volume again reaches 1-2 mL, remove the K-D apparatus from the water batch and allow it to drain and cool for at least 10 minutes.

7.10 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the techniques described in Sec. 7.11 or adjusted to 10.0 mL with the solvent last used.

7.11 If further concentration is indicated in Table 1, either micro Snyder column technique (Sec. 7.11.1) or nitrogen blowdown technique (Sec. 7.11.2) is used to adjust the extract to the final volume required.

7.11.1 Micro Snyder Column Technique

7.11.1.1 Add another one or two clean boiling chips to the concentrator tube and attach a two ball micro Snyder column. Prewet the column by adding about 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints with about 0.2 mL of solvent and add to the

concentrator tube. Adjust the final volume to 1.0-2.0 mL, as indicated in Table 1, with solvent.

7.11.2 Nitrogen Blowdown Technique

7.11.2.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: Do not use plasticized tubing between the carbon trap and the sample.

7.11.2.2 The internal wall of the tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.12 The extracts obtained may now be analyzed for the target analytes using the appropriate organic technique(s) (see Sec. 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store in a refrigerator. If the extract will be stored longer than 2 days, it should be transferred to a vial with a Teflon lined screw cap or crimp top, and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

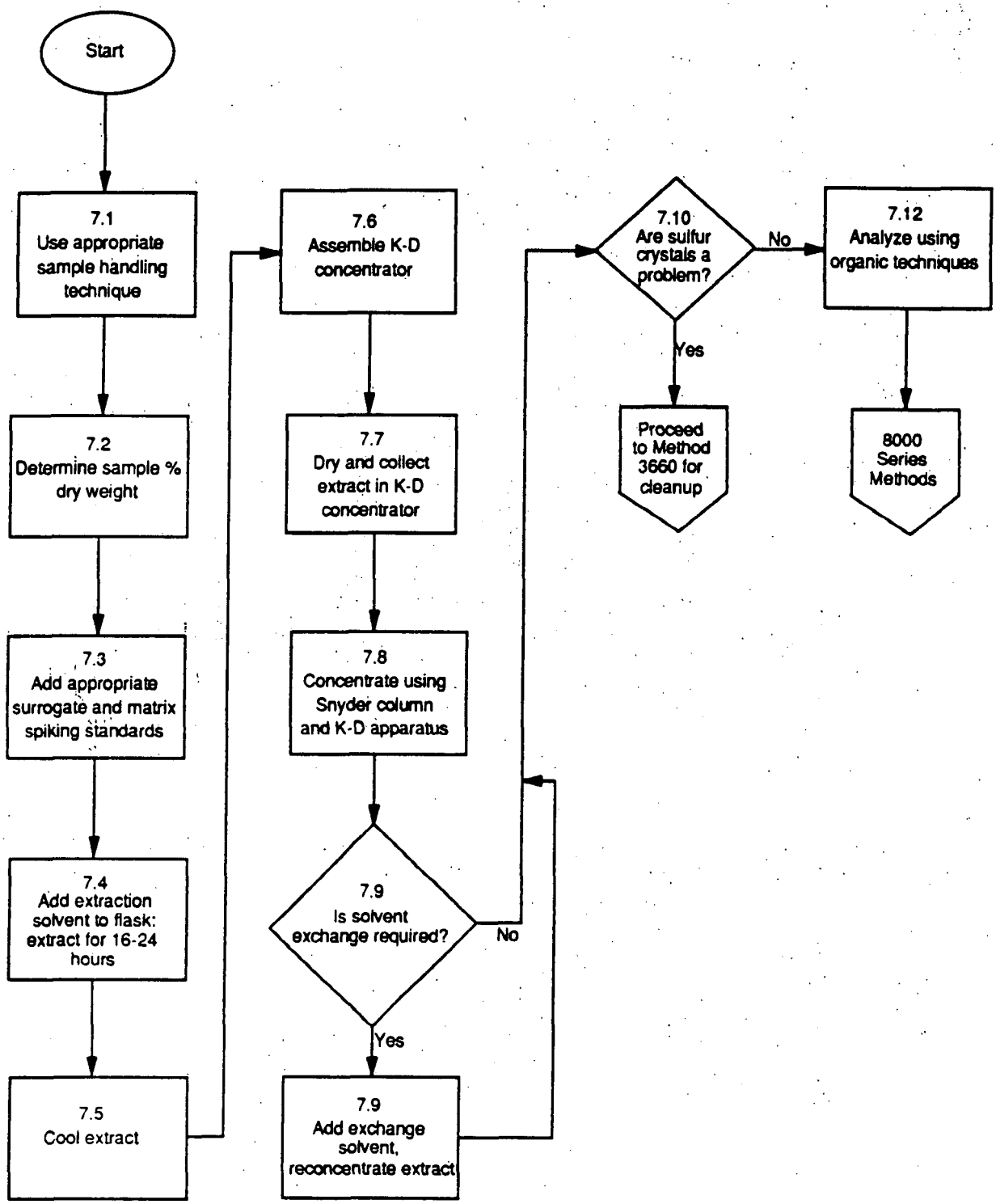
TABLE 1.
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040[a]	as received	2-propanol	hexane	1.0	1.0, 10.0[b]
8060	as received	hexane	hexane	2.0	10.0
8061	as received	hexane	hexane	2.0	10.0
8070	as received	methanol	methylene chloride	2.0	10.0
8080	as received	hexane	hexane	10.0	10.0
8081	as received	hexane	hexane	10.0	10.0
8090	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8110	as received	hexane	hexane	2.0	10.0
8120	as received	hexane	hexane	2.0	1.0
8121	as received	hexane	hexane	2.0	1.0
8140	as received	hexane	hexane	10.0	10.0
8141	as received	hexane	hexane	10.0	10.0
8250[a,c]	as received	none	--	--	1.0
8270[a,c]	as received	none	--	--	1.0
8310	as received	acetonitrile	--	--	1.0
8321	as received	methanol	--	--	1.0
8410	as received	methylene chloride	methylene chloride	10.0	0.0 (dry)

[a] To obtain separate acid and base/neutral extracts, Method 3650 should be performed following concentration of the extract to 10.0 mL.

[b] Phenols may be analyzed by Method 8040 using a 1.0 mL 2-propanol extract and analysis by GC/FID. Method 8040 also contains an optical derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

[c] The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.


Start
7.1 Use appropriate sample handling technique
7.2 Determine sample % dry weight
7.3 Add appropriate surrogate and matrix spiking standards
7.4 Add extraction solvent to flask: extract for 16-24 hours
7.5 Cool extract
7.6 Assemble K-D concentrator
7.7 Dry and collect extract in K-D concentrator
7.8 Concentrate using Snyder column and K-D apparatus
7.9 Is solvent exchange required?
No
Yes
7.9 Add exchange solvent, reconcentrate extract
7.10 Are sulfur crystals a problem?
No
Yes
Proceed to Method 3660 for cleanup
7.12 Analyze using organic techniques
8000 Series Methods

METHOD 3541

AUTOMATED SOXHLET EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 Method 3541 describes the extraction of organic analytes from soil, sediment, sludges, and waste solids. The method uses a commercially available, unique, three stage extraction system to achieve analyte recovery comparable to Method 3540, but in a much shorter time. There are two differences between this extraction method and Method 3540. In the initial extraction stage of Method 3541, the sample-loaded extraction thimble is immersed into the boiling solvent. This ensures very rapid intimate contact between the specimen and solvent and rapid extraction of the organic analytes. In the second stage the thimble is elevated above the solvent, and is rinse-extracted as in Method 3540. In the third stage, the solvent is evaporated, as would occur in the Kuderna-Danish (K-D) concentration step in Method 3540. The concentrated extract is then ready for cleanup (Method 3600) followed by measurement of the organic analytes.

1.2 The method is applicable to the extraction and concentration of water insoluble or slightly water soluble polychlorinated biphenyls (PCBs) in preparation for gas chromatographic determination using either Method 8080 or 8081. This method is applicable to soils, clays, solid wastes and sediments containing from 1 to 50 μg of PCBs (measured as Arochlors) per gram of sample. It has been statistically evaluated at 5 and 50 μg/g of Arochlors 1254 and 1260, and found to be equivalent to Method 3540 (Soxhlet Extraction). Higher concentrations of PCBs are measured following volumetric dilution with hexane.

1.3 The method is also applicable the extraction and concentration of semivolatile organics in preparation for GC/MS analysis by Method 8270 or by analysis using specific GC or HPLC methods.

2.0 SUMMARY OF METHOD

2.1 PCBs: Moist solid samples (e.g., soil/sediment samples) may be air-dried and ground prior to extraction or chemically dried with anhydrous sodium sulfate. The prepared sample is extracted using 1:1 (v/v) acetone:hexane in the automated Soxhlet following the same procedure as outlined for semivolatile organics in Sec. 2.1. The extract is then concentrated and exchanged into pure hexane prior to final gas chromatographic PCB measurement.

2.2 Other semivolatile organics: A 10-g solid sample (the sample is pre-mixed with anhydrous sodium sulfate for certain matrices) is placed in an extraction thimble and usually extracted with 50 mL of 1:1 (v/v) acetone/hexane for 60 minutes in the boiling extraction solvent. The thimble with sample is then raised into the rinse position and extracted for an additional 60 minutes. Following the extraction steps, the extraction solvent is concentrated to 1 to 2 mL.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 The extraction thimble and the o-rings used to seal the extraction cup are both a source of interference. Both should be checked by including a method blank and following the extraction procedure as written. Solvent rinsing or extraction, prior to use, may be necessary to eliminate or reduce interferences. Viton seals contributed least to the interference problem, however, even they contributed some interference peaks when the extraction solvent was analyzed by the electron capture detector. Use of butyl or EPDM rings are not recommended since they were found to contribute significant background when the extraction solvent was 1:1 v/v hexane/acetone or 1:1 v/v methylene chloride/acetone.

4.0 APPARATUS AND MATERIALS

4.1 Automated Soxhlet Extraction System - with temperature-controlled oil bath (Soxtec, or equivalent). Tecator bath oil (catalog number 1000-1886) should be used with the Soxtec. Silicone oil must not be used because it destroys the rubber parts. See Figure 1. The apparatus is used in a hood.

4.2 Accessories and consumables for the automated Soxhlet system. (The catalog numbers are Fisher Scientific based on the use of the Soxtec HT-6, however, other sources that are equivalent are acceptable.)

4.2.1 Cellulose extraction thimbles - 26 mm ID x 60 mm contamination free, catalog number 1522-0034, or equivalent.

4.2.2 Glass extraction cups (80 mL) - (set of six required for the HT-6), catalog number 1000-1820.

4.2.3 Thimble adapters - (set of six required for the HT-6), catalog number 1000-1466.

4.2.4 Viton seals - catalog number 1000-2516.

4.3 Syringes - 100 and 1000 μL and 5 mL.

4.4 Apparatus for Determining Percent Dry Weight

4.4.1 Drying Oven.

4.4.2 Desiccator.

4.4.3 Crucibles, porcelain.

4.4.4 Balance, analytical.

4.5 Apparatus for grinding - Fisher Cyclotec, Fisher Scientific catalog number 1093, or equivalent.

4.6 Spatula

4.7 Graduated cylinder - 100 mL.

4.8 Aluminum weighing dish - VWR Scientific catalog number 25433-008 or equivalent.

4.9 Graduated, conical-bottom glass tubes - 15 mL, Kimble catalog number 45166 or equivalent, or 10 mL KD concentrator tube.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. A method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Extraction solvents:

5.4.1 Organochlorine pesticides/PCB extraction:

5.4.1.1 Acetone/hexane (1:1 v/v), CH_3COCH_3/C_6H_{14}. Pesticide quality or equivalent.

5.4.2 Semivolatile organics extraction:

5.4.2.1 Acetone/hexane (1:1 v/v), CH_3COCH_3/C_6H_{14}. Pesticide quality or equivalent.

5.4.2.2 Acetone/methylene chloride (1:1 v/v), CH_3COCH_3/CH_2Cl_2. Pesticide quality or equivalent.

5.5 Hexane, C_6H_{14}. Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Sample handling

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.1.1 PCBs or high-boiling organochlorine pesticides - Air-dry the sample at room temperature for 48 hours in a glass tray or on hexane-cleaned aluminum foil, or dry the sample by mixing with anhydrous sodium sulfate until a free-flowing powder is obtained (see Sec. 7.2).

NOTE: Dry, finely ground soil/sediment allows the best extraction efficiency for non-volatile, non-polar organics, e.g., PCBs, 4,4'-DDT, etc. Air-drying is not appropriate for the analysis of the more volatile organochlorine pesticides (e.g. the BHCs) or the more volatile of the semivolatile organics because of losses during the drying process.

7.1.2 Dried sediment/soil and dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1 mm sieve or can be extruded through a 1 mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 20 g after grinding. Disassemble grinder between samples, according to manufacturer's instructions, and clean with soap and water, followed by acetone and hexane rinses.

NOTE: The same warning on loss of volatile analytes applies to the grinding process. Grinding should only be performed when analyzing for non-volatile organics.

7.1.3 Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise broken up to allow mixing, and maximum exposure of the sample surfaces for extraction. If grinding of these materials is preferred, the addition and mixing of anhydrous sodium sulfate with the sample (1:1) may improve grinding efficiency. The professional judgment of the analyst is required for handling such difficult matrices.

7.1.4 Multiple phase waste samples - Samples consisting of multiple phases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.2 For sediment/soil (especially gummy clay) that is moist and cannot be air-dried because of loss of volatile analytes - Mix 5 g of sample with 5 g of anhydrous sodium sulfate in a small beaker using a spatula. Use this approach for any solid sample that requires dispersion of the sample particles to ensure greater solvent contact throughout the sample mass.

7.3 Determination of sample percent dry weight - In certain cases, sample results are desired based on dry weight basis. When such data are desired, a portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from the drying of a heavily contaminated hazardous waste sample.

7.3.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.4 Check the heating oil level in the automated Soxhlet unit and add oil if needed. See service manual for details. Set the temperature on the service unit at 140°C when using hexane-acetone (1:1, v/v) as the extraction solvent.

7.5 Press the "MAINS" button; observe that the switch lamp is now "ON".

7.6 Open the cold water tap for the reflux condensers. Adjust the flow to 2 L/min to prevent solvent loss through the condensers.

7.7 Weigh 10 g of sample into extraction thimbles. For samples mixed with anhydrous sodium sulfate, transfer the entire contents of the beaker (Sec. 7.2) to the thimble. Add surrogate spikes to each sample and the matrix spike/matrix spike duplicate to the selected sample.

NOTE: When surrogate spikes and/or matrix spikes contain relatively volatile compounds (e.g., trichlorobenzenes, BHCs, etc.), steps 7.8, 7.9, and 7.10 must be performed quickly to avoid evaporation losses of these compounds. As the spike is added to the sample in each thimble, the thimble should immediately be transferred to the condenser and lowered into the extraction solvent.

7.8 Immediately transfer the thimbles containing the weighed samples into the condensers. Raise the knob to the "BOILING" position. The magnet will now fasten to the thimble. Lower the knob to the "RINSING" position. The thimble will now hang just below the condenser valve.

7.9 Insert the extraction cups containing boiling chips, and load each with 50 mL of extraction solvent (normally 1:1 (v/v) hexane:acetone, see Sec. 5.4). Using the cup holder, lower the locking handle, ensuring that the safety catch engages. The cups are now clamped into position. (The seals must be pre-rinsed or pre-extracted with extraction solvent prior to initial use.)

7.10 Move the extraction knobs to the "BOILING" position. The thimbles are now immersed in solvent. Set the timer for 60 minutes. The condenser valves must be in the "OPEN" position. Extract for the preset time.

7.11 Move the extraction knobs to the "RINSING" position. The thimbles will now hang above the solvent surface. Set timer for 60 minutes. Condenser valves are still open. Extract for the preset time.

7.12 After rinse time has elapsed, close the condenser valves by turning each a quarter-turn, clockwise.

7.13 When all but 2 to 5 mL of solvent have been collected, open the system and remove the cups.

7.14 Transfer the contents of the cups to 15 mL graduated, conical-bottom glass tubes. Rinse the cups using hexane (methylene chloride if 1:1 methylene chloride-acetone was used for extraction and analysis is by GC/MS) and add the rinsates to the glass tubes. Concentrate the extracts to 1 to 10 mL. The final volume is dependent on the determinative method and the quantitation limit required. Transfer a portion to a GC vial and store at 4°C until analyses are performed.

NOTE: The recovery solvent volume can be adjusted by adding solvent at the top of the condensers. For more details concerning use of the extractor, see the operating manual for the automated extraction system.

7.15 Shutdown

7.15.1 Turn "OFF" main switch.

7.15.2 Turn "OFF" cold water tap.

7.15.3 Ensure that all condensers are free of solvent. Empty the solvent that is recovered in the evaporation step into an appropriate storage container.

7.16 The extract is now ready for cleanup or analysis, depending on the extent of interfering co-extractives. See Method 3600 for guidance on cleanup methods and Method 8000 for guidance on determinative methods. Certain cleanup and/or determinative methods may require a solvent exchange prior to cleanup and/or determination.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for general quality control procedures and to Method 3500 for specific extraction and sample preparation QC procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of an organic-free solid matrix (e.g., reagent sand) method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted, or when there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement. This is especially important because of the possibility of interferences being extracted from the extraction cup seal.

8.3 Standard quality assurance practices should be used with this method. Field duplicates should be collected to validate the precision of the sampling technique. Each analysis batch of 20 or less samples must contain: a method blank, either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis, and a laboratory control sample, unless the determinative method provides other guidance. Also, routinely check the integrity of the instrument seals.

8.4 Surrogate standards must be added to all samples when specified in the appropriate determinative method.

9.0 METHOD PERFORMANCE

9.1 Multi-laboratory accuracy and precision data were obtained for PCBs in soil. Eight laboratories spiked Arochlors 1254 and 1260 into three portions of 10 g of Fuller's Earth on three non-consecutive days followed by immediate extraction using Method 3541. Six of the laboratories spiked each Arochlor at 5 and 50 mg/kg and two laboratories spiked each Arochlor at 50 and 500 mg/kg. All extracts were analyzed by Oak Ridge National Laboratory, Oak Ridge, TN, using Method 8081. These data are listed in a table found in Method 8081, and were taken from Reference 1.

9.2 Single-laboratory accuracy data were obtained for chlorinated hydrocarbons, nitroaromatics, haloethers, and organochlorine pesticides in a clay soil. The spiking concentrations ranged from 500 to 5000 µg/kg, depending on the sensitivity of the analyte to the electron capture detector. The spiking solution was mixed into the soil during addition and then immediately transferred to the extraction device and immersed in the extraction solvent. The data represents a single determination. Analysis was by capillary column gas chromatography/electron capture detector following Methods 8081 for the organochlorine pesticides, 8091 for the nitroaromatics, 8111 for the hydrocarbons, and 8121 for the chlorinated hydrocarbons. These data are listed in a table located in their respective methods and were taken from Reference 2.

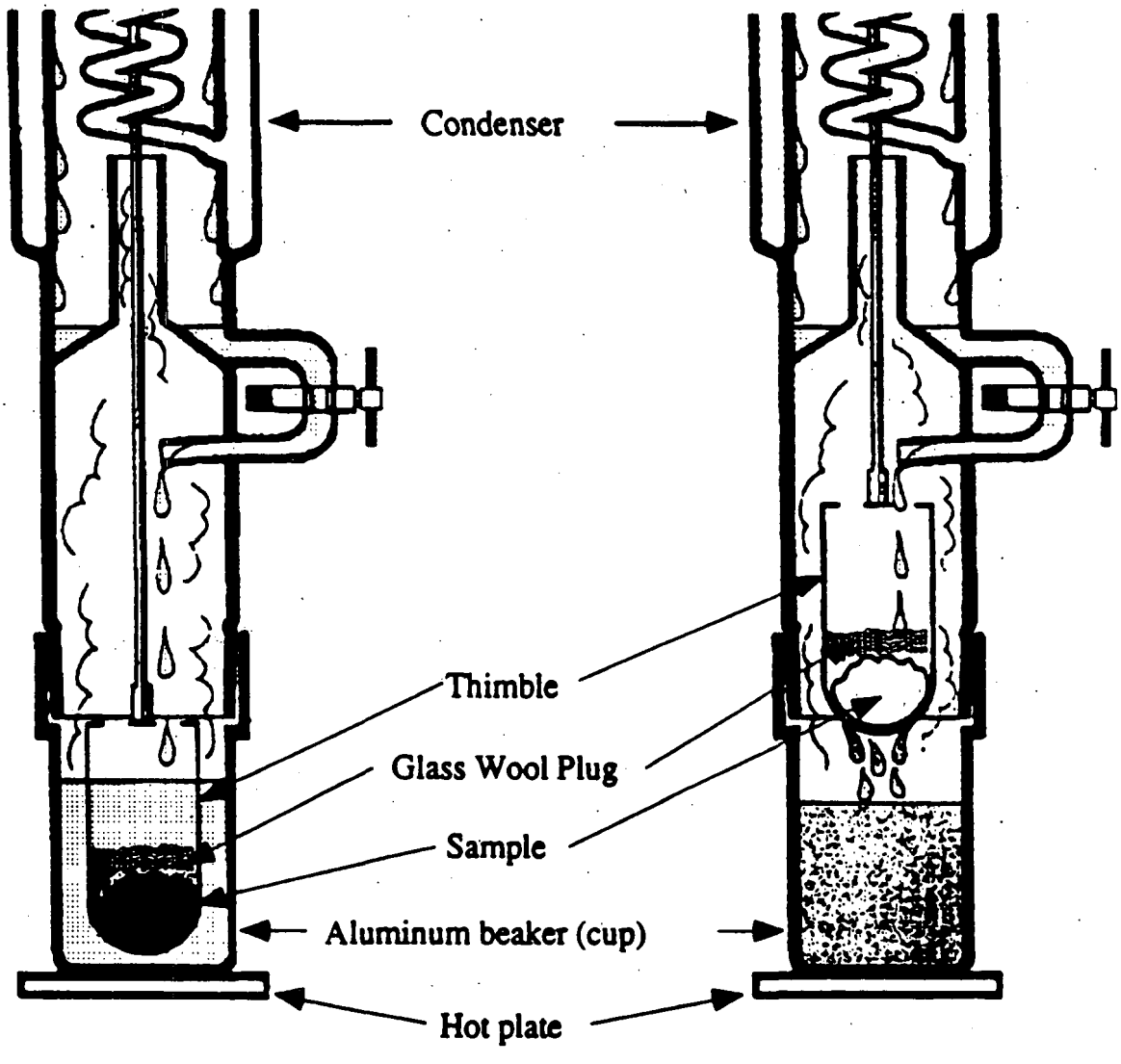
9.3 Single-laboratory accuracy and precision data were obtained for semivolatile organics in soil by spiking at a concentration of 6 mg/kg for each compound. The spiking solution was mixed into the soil during addition and then allowed to equilibrate for approximately 1 hr prior to extraction. Three determinations were performed and each extract was analyzed by gas chromatography/mass spectrometry following Method 8270. The low recovery of the more volatile compounds is probably due to volatilization losses during equilibration. These data are listed in a Table located in Method 8270 and were taken from Reference 2.

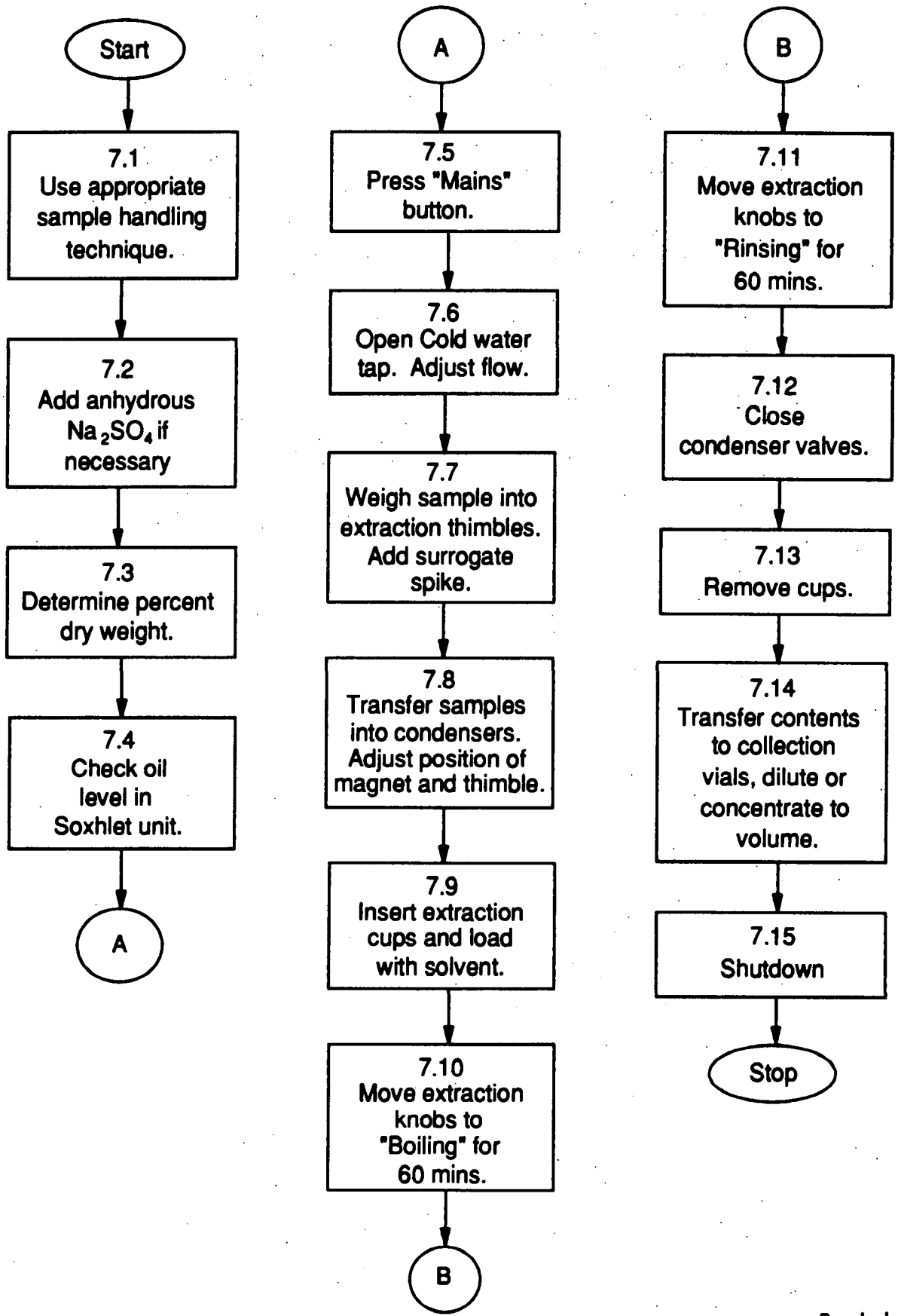
10.0 REFERENCES

1. Stewart, J. "Intra-Laboratory Recovery Data for the PCB Extraction Procedure"; Oak Ridge National Laboratory, Oak Ridge, TN, 37831-6138; October 1989.

2. Lopez-Avila, V. (Beckert, W., Project Officer), "Development of a Soxtec Extraction Procedure for Extracting Organic Compounds from Soils and Sediments", EPA 600/X-91/140, US EPA, Environmental Monitoring Systems Laboratory-Las Vegas, October 1991.

Figure 1
Automated Soxhlet Extraction System




Start
7.1 Use appropriate sample handling technique.
7.2 Add anhydrous Na_2SO_4 if necessary
7.3 Determine percent dry weight.
7.4 Check oil level in Soxhlet unit.
A
A
7.5 Press "Mains" button.
7.6 Open Cold water tap. Adjust flow.
7.7 Weigh sample into extraction thimbles. Add surrogate spike.
7.8 Transfer samples into condensers. Adjust position of magnet and thimble.
7.9 Insert extraction cups and load with solvent.
7.10 Move extraction knobs to "Boiling" for 60 mins.
B
B
7.11 Move extraction knobs to "Rinsing" for 60 mins.
7.12 Close condenser valves.
7.13 Remove cups.
7.14 Transfer contents to collection vials, dilute or concentrate to volume.
7.15 Shutdown
Stop

METHOD 3550

SONICATION EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 Method 3550 is a procedure for extracting nonvolatile and semi-volatile organic compounds from solids such as soils, sludges, and wastes. The sonication process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 The method is divided into two sections, based on the expected concentration of organics in the sample. The low concentration method (individual organic components of $\leq$20 mg/kg) uses a larger sample size and a more rigorous extraction procedure (lower concentrations are more difficult to extract). The high concentration method (individual organic components of >20 mg/kg) is much simpler and therefore faster.

1.3 It is highly recommended that the extracts be cleaned up prior to analysis. See Cleanup, Section 4.2.2 of Chapter Four, for applicable methods.

2.0 SUMMARY OF METHOD

2.1 Low concentration method: A 30-g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted three times using sonication. The extract is separated from the sample by vacuum filtration or centrifugation. The extract is ready for cleanup and/or analysis following concentration.

2.2 High concentration method: A 2-g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted once using sonication. A portion of the extract is removed for cleanup and/or analysis.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Apparatus for grinding: If the sample will not pass through a 1-mm standard sieve or cannot be extruded through a 1-mm opening, it should be processed into a homogeneous sample that meets these requirements. Fisher Mortar Model 155 Grinder, Fisher Scientific Co., Catalogue Number 8-323, or an equivalent brand and model, is recommended for sample processing. This grinder should handle most solid samples, except gummy, fibrous, or oily materials.

4.2 Sonication: A horn-type sonicator equipped with a titanium tip should be used. The following sonicator, or an equivalent brand and model, is recommended:

Ultrasonic cell disrupter: Heat Systems - Ultrasonics, Inc., Model W-385 (475 watt) sonicator or equivalent (Power wattage must be a minimum of 375 with pulsing capability and No. 200 1/2" Tapped Disrupter Horn) plus No. 207 3/4" Tapped Disrupter Horn, and No. 419 1/8" Standard Tapered microtip probe.

4.3 Sonabox: Recommended with above disrupters for decreasing cavitation sound (Heat Systems - Ultrasonics, Inc., Model 432B or equivalent).

4.4 Apparatus for determining percent moisture:

4.4.1 **Oven:** Drying.

4.4.2 **Desiccator.**

4.4.3 **Crucibles:** Porcelain.

4.5 Pasteur glass pipets: Disposable, 1-mL.

4.6 Beakers: 400-mL.

4.7 Vacuum filtration apparatus:

4.7.1 **Buchner funnel.**

4.7.2 **Filter paper:** Whatman No. 41 or equivalent.

4.8 Kuderna-Danish (K-D) apparatus:

4.8.1 **Concentrator tube:** 10-mL graduated (Kontes K-570050-1025 or equivalent).

4.8.2 **Evaporator flask:** 500-mL (Kontes K-570001-0500 or equivalent).

4.8.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.8.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.9 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.10 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.11 Balance: Top-loading, capable of accurately weighing 0.01 g.

4.12 Vials and caps: 2-mL for GC auto-sampler.

4.13 Glass scintillation vials: At least 20-mL, with screw-cap and Teflon or aluminum foil liner.

4.14 Spatula: Stainless steel or Teflon.

4.15 Drying column: 20-mm I.D. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.16 Syringe: 5-mL.

5.0 REAGENTS

5.1 Sodium sulfate: Anhydrous and reagent grade, heated at 400°C for 4 hr, cooled in a desiccator, and stored in a glass bottle. Baker anhydrous powder, catalog #73898, or equivalent.

5.2 Extraction solvents: Methylene chloride:acetone (1:1, v:v), methylene chloride, hexane (pesticide quality or equivalent).

5.3 Exchange solvents: Hexane, 2-propanol, cyclohexane, acetonitrile (pesticide quality or equivalent).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Sample handling:

7.1.1 **Sediment/soil samples:** Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.2 **Waste samples:** Samples consisting of multiphases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.1.3 **Dry waste samples amenable to grinding:** Grind or otherwise subdivide the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.2 Determination of percent moisture: In certain cases, sample results are desired based on a dry-weight basis. When such data is desired, a portion of sample for moisture determination should be weighed out at the same time as the portion used for analytical determination.

7.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\frac{\text{g of sample} - \text{g of dry sample}}{\text{g of sample}} \times 100 = \%\ \text{moisture}$$

7.3 Determination of pH (if required): Transfer 50 g of sample to a 100-mL beaker. Add 50 mL of water and stir for 1 hr. Determine the pH of sample with glass electrode and pH meter while stirring. Discard this portion of sample.

7.4 Extraction method for samples expected to contain low concentrations of organics and pesticides ($\lesssim$20 mg/kg):

7.4.1 The following step should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 g of sample into a 400-mL beaker. Record the weight to the nearest 0.1 g. Non-porous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate using a spatula. The sample should be free-flowing at this point. Add 1 mL of surrogate standards to all samples, spikes, and blanks (see Method 3500 for details on the surrogate standard solution and the matrix spike solution). For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/uL of each base/neutral analyte and 200 ng/uL of each acid analyte in the extract to be analyzed (assuming a 1 uL injection). If Method 3640, Gel-permeation cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half of the extract is lost due to loading of the GPC column. Immediately add 100 mL of 1:1 methylene chloride:acetone.

7.4.2 Place the bottom surface of the tip of the #207 3/4 in. disruptor horn about 1/2 in. below the surface of the solvent, but above the sediment layer.

7.4.3 Sonicate for 3 min, with output control knob set at 10 and with mode switch on Pulse and percent-duty cycle knob set at 50%. Do NOT use microtip probe.

7.4.4 Decant and filter extracts through Whatman No. 41 filter paper using vacuum filtration or centrifuge and decant extraction solvent.

7.4.5 Repeat the extraction two or more times with two additional 100-mL portions of solvent. Decant off the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with extraction solvent.

7.4.6 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask.

7.4.7 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Wash the extractor flask and sodium sulfate column with 100-125 mL of extraction solvent to complete the quantitative transfer.

7.4.8 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-15 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.4.9 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip, and re-attach the Snyder column. Concentrate the extract as described in Paragraph 7.4.8, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.4.10 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Paragraph 7.4.11 or adjusted to 10.0 mL with the solvent last used.

7.4.11 Add a clean boiling chip and attach a two-ball micro-Snyder column to the concentrator tube. Prewet the column by adding approximately 0.5 mL of methylene chloride or exchange solvent through the top. Place the apparatus in the hot water bath. Adjust the vertical position and the water temperature, as required, to complete the concentration in 5-10 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the liquid

TABLE 1. SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040[a]	as received	2-propanol	hexane	1.0	1.0, 10.0[b]
8060	as received	hexane	hexane	2.0	10.0
8080	as received	hexane	hexane	10.0	10.0
8090	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8120	as received	hexane	hexane	2.0	1.0
8140	as received	hexane	hexane	10.0	10.0
8250[a,c]	as received	none	-	-	1.0
8270[a,c]	as received	none	-	-	1.0
8310	as received	acetonitrile	-	-	1.0

[a]To obtain separate acid and base/neutral extracts, Method 3650 should be performed following concentration of the extract to 10.0 mL.

[b]Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

[c]The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

reaches an apparent volume of approximately 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 min. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with approximately 0.2 mL of appropriate solvent. Adjust the final volume to the volume required for cleanup or for the determinative method (see Table 1).

7.4.12 Transfer the concentrated extract to a clean screw-cap vial. Seal the vial with a Teflon-lined lid and mark the level on the vial. Label with the sample number and fraction and store in the dark at 4°C until ready for analysis or cleanup.

7.5 Extraction method for samples expected to contain high concentrations of organics (>20 mg/kg):

7.5.1 Transfer approximately 2 g (record weight to the nearest 0.1 g) of sample to a 20-mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of sample taken. Cap the vial before proceeding with the next sample to avoid any cross contamination.

7.5.2 Add 2 g of anhydrous sodium sulfate to sample in the 20-mL vial and mix well.

7.5.3 Surrogate standards are added to all samples, spikes, and blanks (see Method 3500 for details on the surrogate standard solution and on the matrix spike solution). Add 2.0 mL of surrogate spiking solution to sample mixture. For the sample in each analytical batch selected for spiking, add 2.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 200 ng/uL of each base/neutral analyte and 400 ng/uL of each acid analyte in the extract to be analyzed (assuming a 1 uL injection). If Method 3640, Gel-permeation cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.5.4 Immediately add whatever volume of solvent is necessary to bring the final volume to 10.0 mL considering the added volume of surrogates and matrix spikes. Disrupt the sample with the 1/8-in. tapered microtip ultrasonic probe for 2 min at output control setting 5 and with mode switch on pulse and percent duty cycle of 50%. Extraction solvents are:

1. Nonpolar compounds, i.e., organochlorine pesticides and PCBs: hexane.

2. Extractable priority pollutants: methylene chloride.

7.5.5 Loosely pack disposable Pasteur pipets with 2- to 3-cm Pyrex glass-wool plugs. Filter the extract through the glass wool and collect

5.0 mL in a concentrator tube if further concentration is required. Follow Paragraphs 7.4.6 through 7.4.12 for details on concentration. Normally, the 5.0 mL extract is concentrated to 1.0 mL.

7.5.6 The extract is ready for cleanup or analysis, depending on the extent of interfering co-extractives.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subject to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

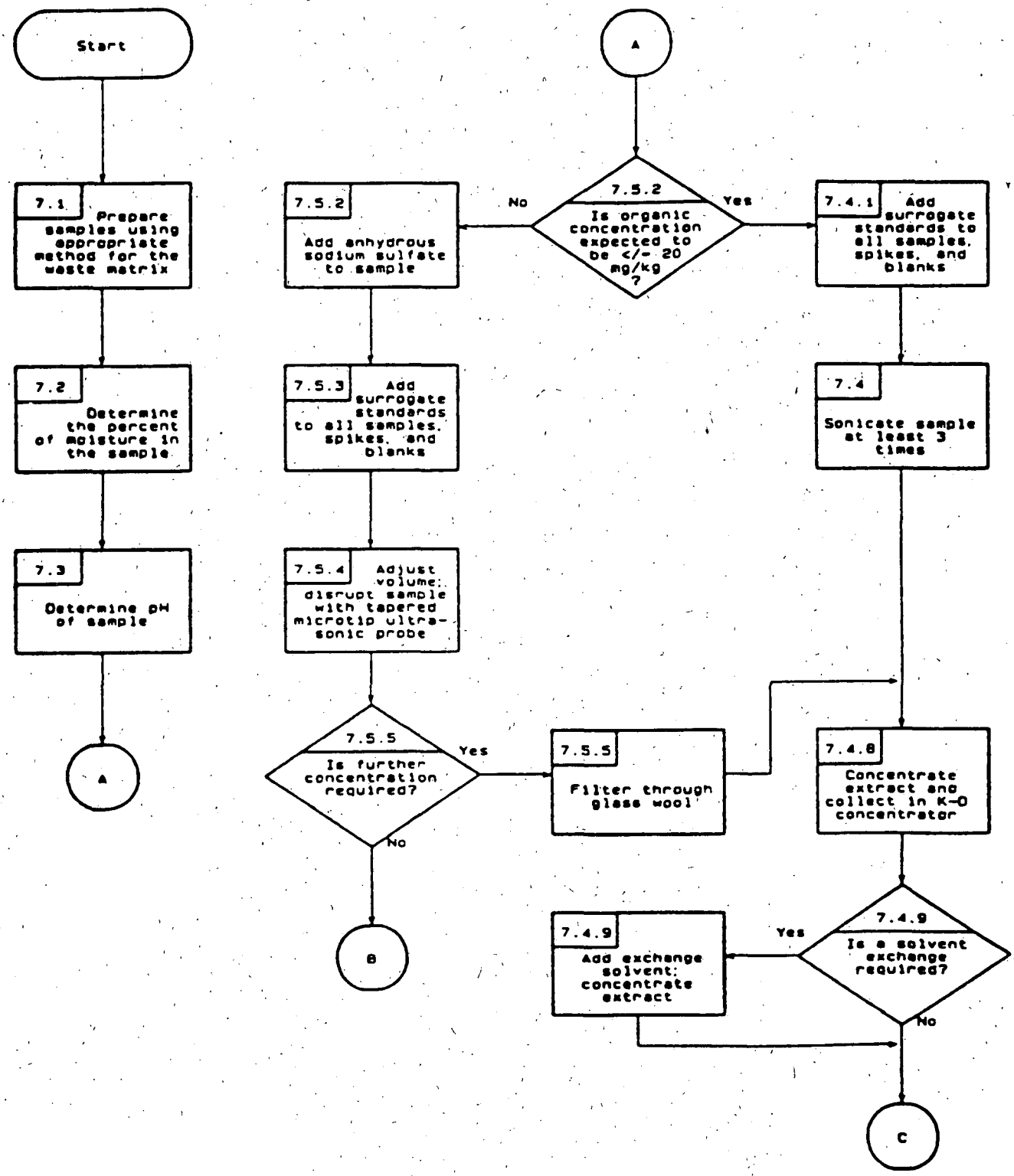
9.0 METHOD PERFORMANCE

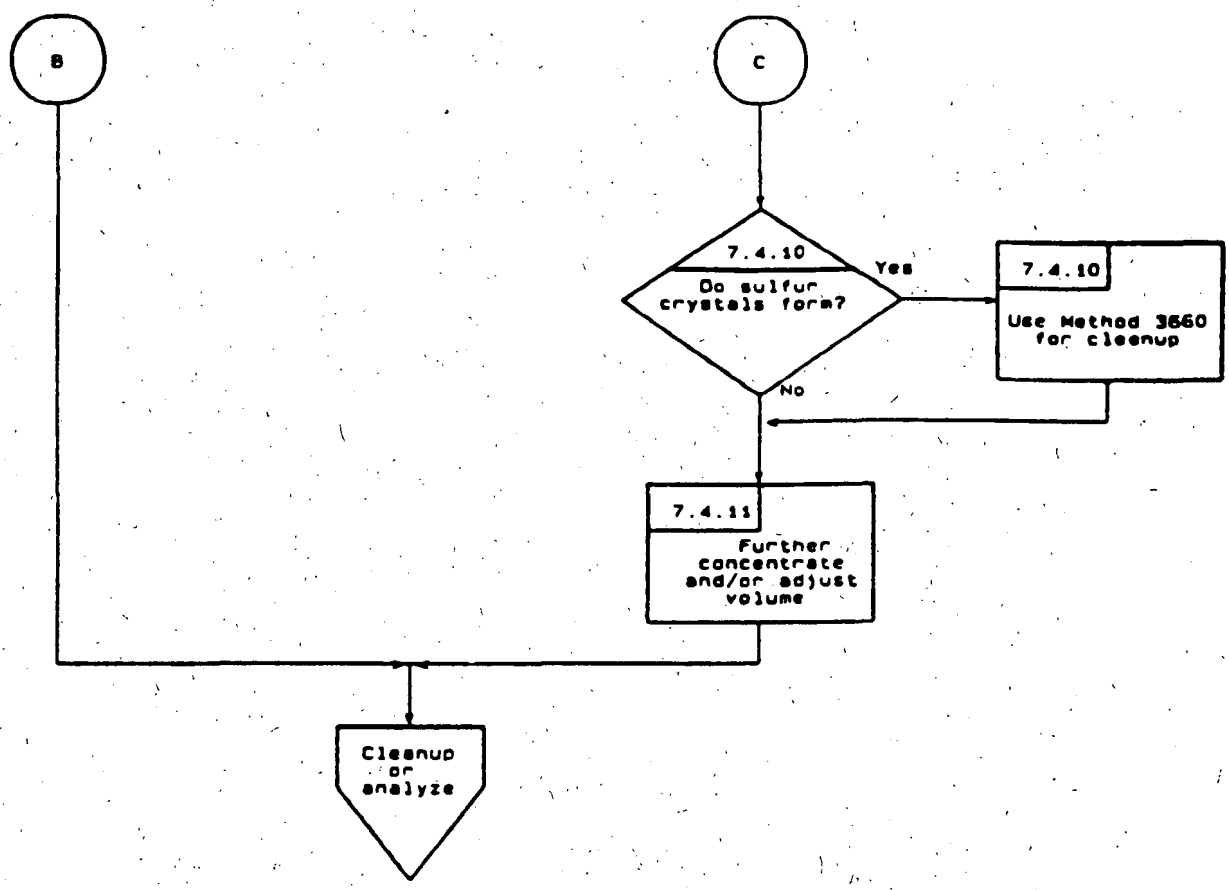
9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

2. U.S. EPA, Interlaboratory Comparison Study: Methods for Volatile and Semi-Volatile Compounds, Environmental Monitoring Systems Laboratory, Office of Research and Development, Las Vegas, NV, EPA 600/4-84-027, 1984.


Start
7.1 Prepare samples using appropriate method for the waste matrix
7.2 Determine the percent of moisture in the sample
7.3 Determine pH of sample
A
A
7.5.2 Is organic concentration expected to be <= 20 mg/kg ?
No
Yes
7.5.2 Add anhydrous sodium sulfate to sample
7.5.3 Add surrogate standards to all samples, spikes, and blanks
7.5.4 Adjust volume; disrupt sample with tapered microtip ultra-sonic probe
7.5.5 Is further concentration required?
Yes
No
B
7.5.5 Filter through glass wool
7.4.1 Add surrogate standards to all samples, spikes, and blanks
7.4 Sonicate sample at least 3 times
7.4.8 Concentrate extract and collect in K-D concentrator
7.4.9 Is a solvent exchange required?
Yes
No
7.4.9 Add exchange solvent; concentrate extract
C


B
C
7.4.10
Do sulfur crystals form?
Yes
No
7.4.10
Use Method 3660 for cleanup
7.4.11
Further concentrate and/or adjust volume
Cleanup or analyze

METHOD 3550A

ULTRASONIC EXTRACTION

See DISCLAIMER-1. See manufacturer's specifications for operational settings.

1.0 SCOPE AND APPLICATION

1.1 Method 3550 is a procedure for extracting nonvolatile and semi-volatile organic compounds from solids such as soils, sludges, and wastes. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 The method is divided into two sections, based on the expected concentration of organics in the sample. The low concentration method (individual organic components of $\leq$ 20 mg/kg) uses a larger sample size and a more rigorous extraction procedure (lower concentrations are more difficult to extract). The medium/high concentration method (individual organic components of > 20 mg/kg) is much simpler and therefore faster.

1.3 It is highly recommended that the extracts be cleaned up prior to analysis. See Chapter Four (Cleanup), Sec. 4.2.2, for applicable methods.

2.0 SUMMARY OF METHOD

2.1 Low concentration method - A 30 g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted three times using ultrasonic extraction. The extract is separated from the sample by vacuum filtration or centrifugation. The extract is ready for cleanup and/or analysis following concentration.

2.2 Medium/high concentration method - A 2 g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted once using ultrasonic extraction. A portion of the extract is removed for cleanup and/or analysis.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Apparatus for grinding dry waste samples.

4.2 Ultrasonic preparation - A horn type device equipped with a titanium tip, or a device that will give equivalent performance, shall be used.

4.2.1 Ultrasonic Disrupter - The disrupter must have a minimum power wattage of 300 watts, with pulsing capability. A device designed to reduce the cavitation sound is recommended. Follow the manufacturers instructions for preparing the disrupter for extraction of samples with low and medium/high concentration.

Use a 3/4" horn for the low concentration method and a 1/8" tapered microtip attached to a 1/2" horn for the medium/high concentration method.

4.3 Sonabox - Recommended with above disrupters for decreasing cavitation sound (Heat Systems - Ultrasonics, Inc., Model 432B or equivalent).

4.4 Apparatus for determining percent dry weight.

4.4.1 Oven - Drying.

4.4.2 Desiccator.

4.4.3 Crucibles - Porcelain or disposable aluminum.

4.5 Pasteur glass pipets - 1 mL, disposable.

4.6 Beakers - 400 mL.

4.7 Vacuum or pressure filtration apparatus.

4.7.1 Buchner funnel.

4.7.2 Filter paper - Whatman No. 41 or equivalent.

4.8 Kuderna-Danish (K-D) apparatus.

4.8.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.8.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.8.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.8.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.8.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.9 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.10 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The batch should be used in a hood.

4.11 Balance - Top loading, capable of accurately weighing to the nearest 0.01 g.

4.12 Vials - 2 mL, for GC autosampler, with Teflon lined screw caps or crimp tops.

4.13 Glass scintillation vials - 20 mL, with Teflon lined screw caps.

4.14 Spatula - Stainless steel or Teflon.

4.15 Drying column - 20 mm ID Pyrex chromatographic column with Pyrex glass wool at bottom.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.16 Syringe - 5 mL.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise specified, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Extraction solvents.

5.4.1 Low concentration soil/sediment and aqueous sludge samples shall be extracted using a solvent system that gives optimum, reproducible recovery for the matrix/analyte combination to be measured. Suitable solvent choices are given in Table 1.

5.4.2 Methylene chloride:Acetone, CH_2Cl_2:CH_3COCH_3 (1:1, v:v). Pesticide quality or equivalent.

5.4.3 Methylene chloride, CH_2Cl_2. Pesticide quality or equivalent.

5.4.4 Hexane, C_6H_{14}. Pesticide quality or equivalent.

5.5 Exchange solvents.

5.5.1 Hexane, C_6H_{14}. Pesticide quality or equivalent.

5.5.2 2-Propanol, $(CH_3)_2CHOH$. Pesticide quality or equivalent.

5.5.3 Cyclohexane, C_6H_{12}. Pesticide quality or equivalent.

5.5.4 Acetonitrile, CH_3CN. Pesticide quality or equivalent.

5.5.5 Methanol, CH_3OH. Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this Chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Sample handling

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.1.2 Determine the dry weight of the sample (Sec. 7.2) remaining after decanting. Measurement of soil pH may be required.

7.1.2 Waste samples - Samples consisting of multiphases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.1.3 Dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1 mm sieve or can be extruded through a 1 mm hole. Introduce sufficient sample into the grinder to yield at least 100 g after grinding.

7.1.4 Gummy, fibrous or oily materials not amenable to grinding should be cut, shredded, or otherwise broken up to allow mixing, and maximum exposure of the sample surfaces for extraction. The professional judgment of the analyst is required for handling of these difficult matrices.

7.2 Determination of percent dry weight - In certain cases, sample results are desired based on a dry weight basis. When such data are desired, or required, a portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from drying a heavily contaminated hazardous waste sample.

However, samples known or suspected to contain significant concentrations of toxic, flammable, or explosive constituents should not be overdried because of concerns for personal safety. Laboratory discretion is advised. It may be prudent to delay overdrying of the weighed-out portion until other analytical results are available.

7.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.3 Extraction method for samples expected to contain low concentrations of organics and pesticides ($\leq$ 20 mg/kg):

7.3.1 The following step should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 g of sample into a 400 mL beaker. Record the weigh to the nearest 0.1 g. Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate, using a spatula. If required, more sodium sulfate may be added. After addition of sodium sulfate, the sample should be free flowing. Add 1 mL of surrogate standards to all samples, spikes, standards, and blanks (see Method 3500 for details on the surrogate standard solution and the matrix spike solution). For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/μL of each base/neutral analyte and 200 ng/μL of each acid analyte in the extract to be analyzed (assuming a 1 μL injection). If Method 3640, Gel-Permeation Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half of the extract is lost due to loading of the GPC column. Immediately add 100 mL of 1:1 methylene chloride:acetone.

7.3.2 Place the bottom surface of the tip of the #207 3/4 in. disrupter horn about 1/2 in. below the surface of the solvent, but above the sediment layer.

7.3.3 Extract ultrasonically for 3 minutes, with output control knob set at 10 (full power) and with mode switch on Pulse (pulsing energy

rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time). Do not use microtip probe.

7.3.4 Decant the extract and filter it through Whatman No. 41 filter paper (or equivalent) in a Buchner funnel that is attached to a clean 500 mL filtration flask. Alternatively, decant the extract into a centrifuge bottle and centrifuge at low speed to remove particles.

7.3.5 Repeat the extraction two or more times with two additional 100 mL portions of solvent. Decant off the solvent after each ultrasonic extraction. On the final ultrasonic extraction, pour the entire sample into the Buchner funnel and rinse with extraction solvent. Apply a vacuum to the filtration flask, and collect the solvent extract. Continue filtration until all visible solvent is removed from the funnel, but do not attempt to completely dry the sample, as the continued application of a vacuum may result in the loss of some analytes. Alternatively, if centrifugation is used in Sec. 7.3.4, transfer the entire sample to the centrifuge bottle. Centrifuge at low speed, and then decant the solvent from the bottle.

7.3.6 Assemble a Kuderna-Danish (K-D) concentrator (if necessary) by attaching a 10 mL concentrator tube to a 500 mL evaporator flask. Transfer filtered extract to a 500 mL evaporator flask and proceed to the next section.

7.3.7 Add one to two clean boiling chips to the evaporation flask, and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80-90 °C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-15 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.3.8 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip, and re-attach the Snyder column. Concentrate the extract as described in Sec. 7.3.10, raising the temperature of the water bath, if necessary, to maintain proper distillation. When the apparent volume again reaches 1-2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.3.9 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Sec. 7.3.10 or adjusted to 10.0 mL with the solvent last used.

7.3.10 If further concentration is indicated in Table 1, either micro Snyder column technique (Sec. 7.3.10.1) or nitrogen blow down technique (Sec. 7.3.10.2) is used to adjust the extract to the final volume required.

7.3.10.1 Micro Snyder Column Technique

7.3.10.1.1 Add a clean boiling chip and attach a two ball micro Snyder column to the concentrator tube. Prewet the column by adding approximately 0.5 mL of methylene chloride or exchange solvent through the top. Place the apparatus in the hot water bath. Adjust the vertical position and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the liquid reaches an apparent volume of approximately 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes. Remove the micro Snyder column and rinse its lower joint with approximately 0.2 mL of appropriate solvent and add to the concentrator tube. Adjust the final volume to the volume required for cleanup or for the determinative method (see Table 1).

7.3.10.2 Nitrogen Blowdown Technique

7.3.10.2.1 Place the concentrator tube in a warm water bath (approximately 35 °C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

<u>CAUTION:</u> Do not use plasticized tubing between the carbon trap and the sample.

7.3.10.2.2 The internal wall of the tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

<u>CAUTION</u>: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.4 If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days, it should be transferred to a vial with a Teflon lined cap and labeled appropriately.

7.5 Extraction method for samples expected to contain high concentrations of organics (> 20 mg/kg):

7.5.1 Transfer approximately 2 g (record weight to the nearest 0.1 g) of sample to a 20 mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of sample taken. Cap the vial before proceeding with the next sample to avoid any cross contamination.

7.5.2 Add 2 g of anhydrous sodium sulfate to sample in the 20 mL vial and mix well.

7.5.3 Surrogate standards are added to all samples, spikes, and blanks (see Method 3500 for details on the surrogate standard solution and on the matrix spike solution). Add 1.0 mL of surrogate spiking solution to sample mixture. For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/μL of each base/neutral analyte and 200 ng/μL of each acid analyte in the extract to be analyzed (assuming a 1 μL injection). If Method 3640, Gel-Permeation Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.5.4 Immediately add whatever volume of solvent is necessary to bring the final volume to 10.0 mL considering the added volume of surrogates and matrix spikes. Disrupt the sample with the 1/8 in. tapered microtip ultrasonic probe for 2 minutes at output control setting 5 and with mode switch on pulse and percent duty cycle at 50%. Extraction solvents are:

1. For nonpolar compounds (i.e., organochlorine pesticides and PCBs), use hexane or appropriate solvent.

2. For extractable priority pollutants, use methylene chloride.

7.5.5 Loosely pack disposable Pasteur pipets with 2 to 3 cm Pyrex glass wool plugs. Filter the extract through the glass wool and collect 5.0 mL in a concentrator tube if further concentration is required. Follow Sec. 7.3.10 for details on concentration. Normally, the 5.0 mL extract is concentrated to approximately 1.0 mL or less.

7.5.6 The extract is ready for cleanup or analysis, depending on the extent of interfering co-extractives.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative method for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

2. U.S. EPA, Interlaboratory Comparison Study: Methods for Volatile and Semi-Volatile Compounds, Environmental Monitoring Systems Laboratory, Office of Research and Development, Las Vegas, NV, EPA 600/4-84-027, 1984.

3. Christopher S. Hein, Paul J. Marsden, Arthur S. Shurtleff, "Evaluation of Methods 3540 (Soxhlet) and 3550 (Sonication) for Evaluation of Appendix IX Analytes form Solid Samples", S-CUBED, Report for EPA Contract 68-03-33-75, Work Assignment No. 03, Document No. SSS-R-88-9436, October 1988.

TABLE 1.
EFFICIENCY OF EXTRACTION SOLVENT SYSTEMS[a]

Solvent System[d]			A		B		C		D		E	
Compound	CAS No.[b]	ABN[c]	%R	SD	%R	SD	%R	SD	%R	SD	%R	SD
4-Bromophenyl phenyl ether	101-55-3	N	64.2	6.5	56.4	0.5	86.7	1.9	84.5	0.4	73.4	1.0
4-Chloro-3-methylphenol	59-50-7	A	66.7	6.4	74.3	2.8	97.4	3.4	89.4	3.8	84.1	1.6
bis(2-Chloroethoxy)methane	111-91-1	N	71.2	4.5	58.3	5.4	69.3	2.4	74.8	4.3	37.5	5.8
bis(2-Chloroethyl) ether	111-44-4	N	42.0	4.8	17.2	3.1	41.2	8.4	61.3	11.7	4.8	1.0
2-Chloronaphthalene	91-58-7	N	86.4	8.8	78.9	3.2	100.8	3.2	83.0	4.6	57.0	2.2
4-Chlorophenyl phenyl ether	7005-72-3	N	68.2	8.1	63.0	2.5	96.6	2.5	80.7	1.0	67.8	1.0
1,2-Dichlorobenzene	95-50-1	N	33.3	4.5	15.8	2.0	27.8	6.5	53.2	10.1	2.0	1.2
1,3-Dichlorobenzene	541-73-1	N	29.3	4.8	12.7	1.7	20.5	6.2	46.8	10.5	0.6	0.6
Diethyl phthalate	84-66-2	N	24.8	1.6	23.3	0.3	121.1	3.3	99.0	4.5	94.8	2.9
4,6-Dinitro-o-cresol	534-52-1	A	66.1	8.0	63.8	2.5	74.2	3.5	55.2	5.6	63.4	2.0
2,4-Dinitrotoluene	121-14-2	N	68.9	1.6	65.6	4.9	85.6	1.7	68.4	3.0	64.9	2.3
2,6-Dinitrotoluene	606-20-2	N	70.0	7.6	68.3	0.7	88.3	4.0	65.2	2.0	59.8	0.8
Heptachlor epoxide	1024-57-3	N	65.5	7.8	58.7	1.0	86.7	1.0	84.8	2.5	77.0	0.7
Hexachlorobenzene	118-74-1	N	62.1	8.8	56.5	1.2	95.8	2.5	89.3	1.2	78.1	4.4
Hexachlorobutadiene	87-68-3	N	55.8	8.3	41.0	2.7	63.4	4.1	76.9	8.4	12.5	4.6
Hexachlorocyclopentadiene	77-47-4	N	26.8	3.3	19.3	1.8	35.5	6.5	46.6	4.7	9.2	1.7
Hexachloroethane	67-72-1	N	28.4	3.8	15.5	1.6	31.1	7.4	57.9	10.4	1.4	1.2
5-Nitro-o-toluidine	99-55-8	B	52.6	26.7	64.6	4.7	74.7	4.7	27.9	4.0	34.0	4.0
Nitrobenzene	98-95-3	N	59.8	7.0	38.7	5.5	46.9	6.3	60.6	6.3	13.6	3.2
Phenol	108-95-2	A	51.6	2.4	52.0	3.3	65.6	3.4	65.5	2.1	50.0	8.1
1,2,4-Trichlorobenzene	120-82-1	N	66.7	5.5	49.9	4.0	73.4	3.6	84.0	7.0	20.0	3.2

[a] Percent recovery of analytes spiked at 200 mg/kg into NIST sediment SRM 1645
[b] Chemical Abstracts Service Registry Number
[c] Compound Type: A = Acid, B = Base, N = neutral
[d] A = Methylene chloride
B = Methylene chloride/Acetone (1/1)
C = Hexane/Acetone (1/1)
D = Methyl t-butyl ether
E = Methyl t-butyl ether/Methanol (2/1)

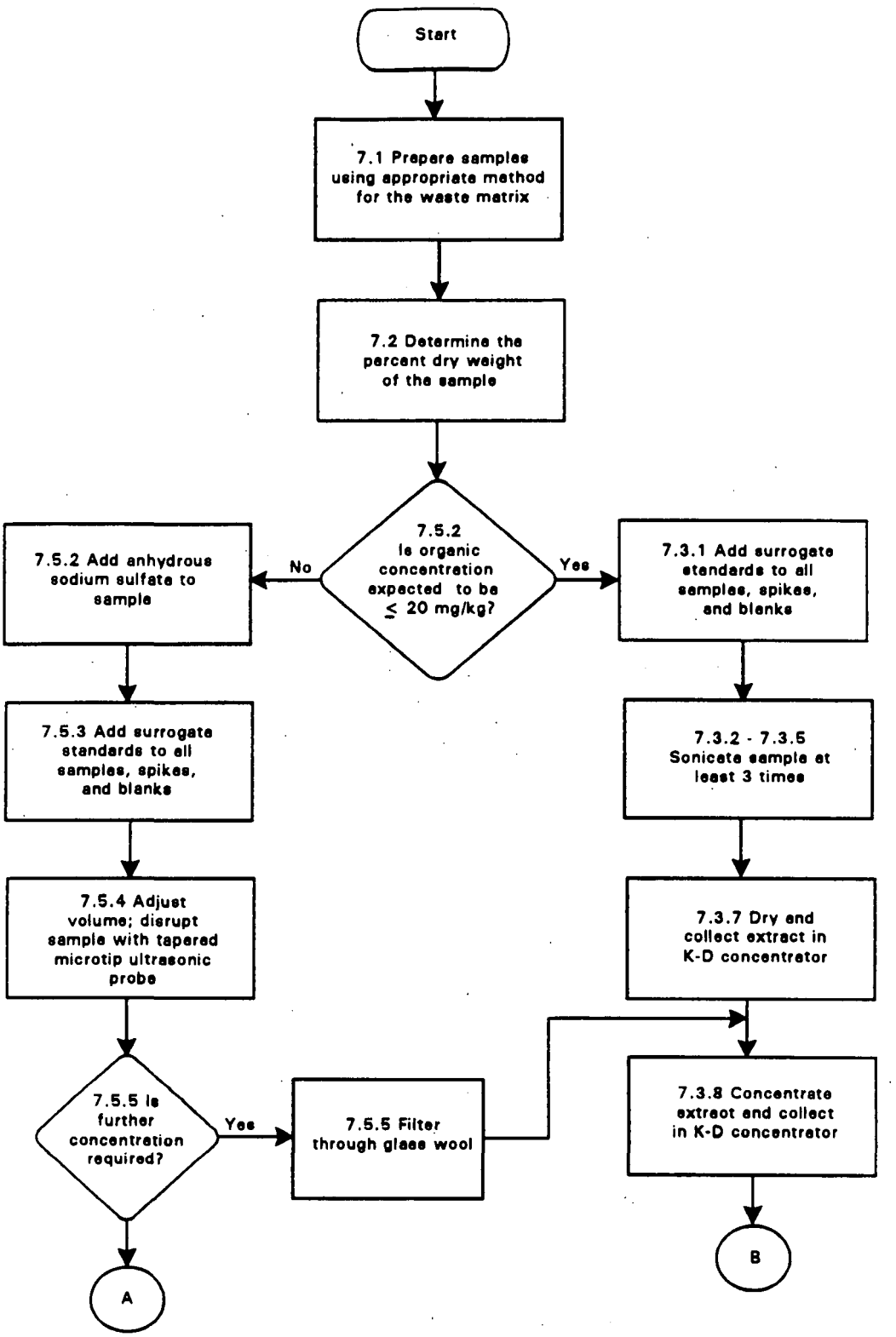
TABLE 2.
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

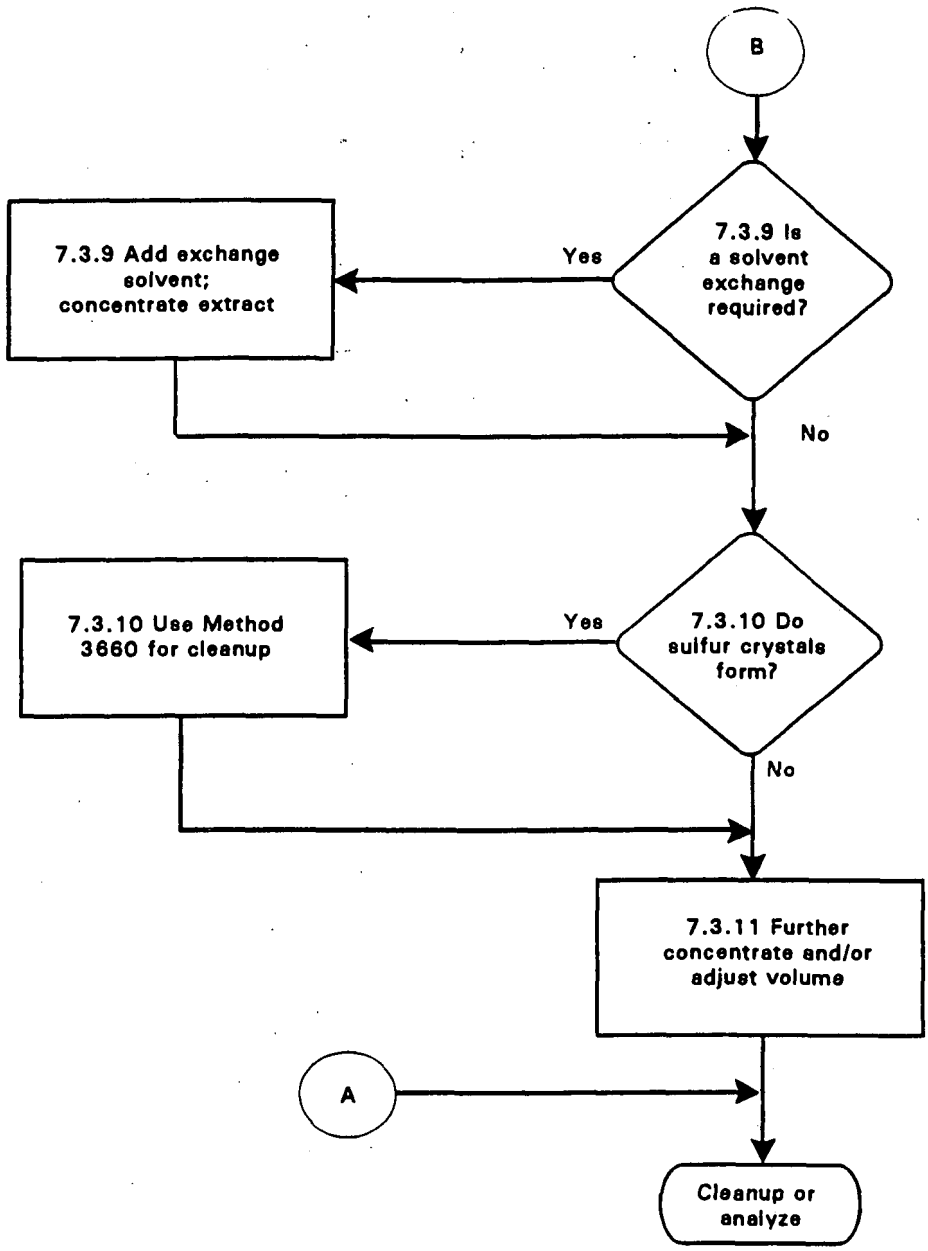
Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040[a]	as received	2-propanol	hexane	1.0	1.0, 10.0[b]
8060	as received	hexane	hexane	2.0	10.0
8061	as received	hexane	hexane	2.0	10.0
8070	as received	methanol	methylene chloride	2.0	10.0
8080	as received	hexane	hexane	10.0	10.0
8081	as received	hexane	hexane	10.0	10.0
8090	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8110	as received	hexane	hexane	2.0	10.0
8120	as received	hexane	hexane	2.0	1.0
8121	as received	hexane	hexane	2.0	1.0
8250[a,c]	as received	none	--	--	1.0
8270[c]	as received	none	--	--	1.0
8310	as received	acetonitrile	--	--	1.0
8321	as received	methanol	--	--	1.0
8410	as received	methylene chloride	methylene chloride	10.0	0.0 (dry)

[a] To obtain separate acid and base/neutral extracts, Method 3650 should be performed following concentration of the extract to 10.0 mL.

[b] Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optical derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

[c] The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.


Start
7.1 Prepare samples using appropriate method for the waste matrix
7.2 Determine the percent dry weight of the sample
7.5.2 Is organic concentration expected to be ≤ 20 mg/kg?
No
Yes
7.5.2 Add anhydrous sodium sulfate to sample
7.3.1 Add surrogate standards to all samples, spikes, and blanks
7.5.3 Add surrogate standards to all samples, spikes, and blanks
7.3.2 - 7.3.5 Sonicate sample at least 3 times
7.5.4 Adjust volume; disrupt sample with tapered microtip ultrasonic probe
7.3.7 Dry and collect extract in K-D concentrator
7.5.5 Is further concentration required?
Yes
7.5.5 Filter through glass wool
7.3.8 Concentrate extract and collect in K-D concentrator
A
B


B
7.3.9 Is a solvent exchange required?
Yes
7.3.9 Add exchange solvent; concentrate extract
No
7.3.10 Do sulfur crystals form?
Yes
7.3.10 Use Method 3660 for cleanup
No
7.3.11 Further concentrate and/or adjust volume
A
Cleanup or analyze

METHOD 3580A

WASTE DILUTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a solvent dilution of a non-aqueous waste sample prior to cleanup and/or analysis. It is designed for wastes that may contain organic chemicals at a concentration greater than 20,000 mg/kg and that are soluble in the dilution solvent.

1.2 It is recommended that an aliquot of the diluted sample be cleaned up. See this chapter, Organic Analytes, Section 4.2.2 (Cleanup).

2.0 SUMMARY OF METHOD

2.1 One gram of sample is weighed into a capped tube, and the sample is diluted to 10.0 mL with an appropriate solvent.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Glass scintillation vials: At least 20 mL, with Teflon or aluminum foil lined screw-cap, or equivalent.

4.2 Spatula: Stainless steel or Teflon.

4.3 Balance: Capable of weighing 100 g to the nearest 0.01 g.

4.4 Vials and caps: 2 mL for GC autosampler.

4.5 Disposable pipets: Pasteur.

4.6 Test tube rack.

4.7 Pyrex glass wool.

4.8 Volumetric flasks, Class A: 10 mL (optional).

5.0 REAGENTS

5.1 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride,

a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.2 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.3 Hexane, C_6H_{14} - Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Samples consisting of multiphases must be prepared by the phase separation method (Chapter Two) before extraction.

7.2 The sample dilution may be performed in a 10 mL volumetric flask. If disposable glassware is preferred, the 20 mL scintillation vial may be calibrated for use. Pipet 10.0 mL of extraction solvent into the scintillation vial and mark the bottom of the meniscus. Discard this solvent.

7.3 Transfer approximately 1 g of each phase of the sample to separate 20 mL vials or 10 mL volumetric flasks (record weight to the nearest 0.1 g). Wipe the mouth of the vial with a tissue to remove any sample material. Cap the vial before proceeding with the next sample to avoid any cross-contamination.

7.4 Add 2.0 mL surrogate spiking solution to all samples and blanks. For the sample in each analytical batch selected for spiking, add 2.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 200 ng/μL of each base/neutral analyte and 400 ng/μL of each acid analyte in the extract to be analyzed (assuming a 1 μL injection). If Method 3640, Gel-permeation cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column. See Method 3500 and the determinative method to be used for details on the surrogate standard and matrix spiking solutions.

7.5 Immediately dilute to 10 mL with the appropriate solvent. For compounds to be analyzed by GC/ECD, e.g., organochlorine pesticides and PCBs, the dilution solvent should be hexane. For base/neutral and acid semivolatile priority pollutants, use methylene chloride. If the dilution is to be cleaned up by gel permeation chromatography (Method 3640), use methylene chloride as the dilution solvent for all compounds.

7.6 Add 2.0 g of anhydrous sodium sulfate to the sample.

7.7 Cap and shake the sample for 2 min.

7.8 Loosely pack disposable Pasteur pipets with 2-3 cm glass wool plugs. Filter the extract through the glass wool and collect 5 mL of the extract in a tube or vial.

7.9 The extract is ready for cleanup or analysis, depending on the extent of interfering co-extractives.

8.0 QUALITY CONTROL

8.1 Any reagent blanks and matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

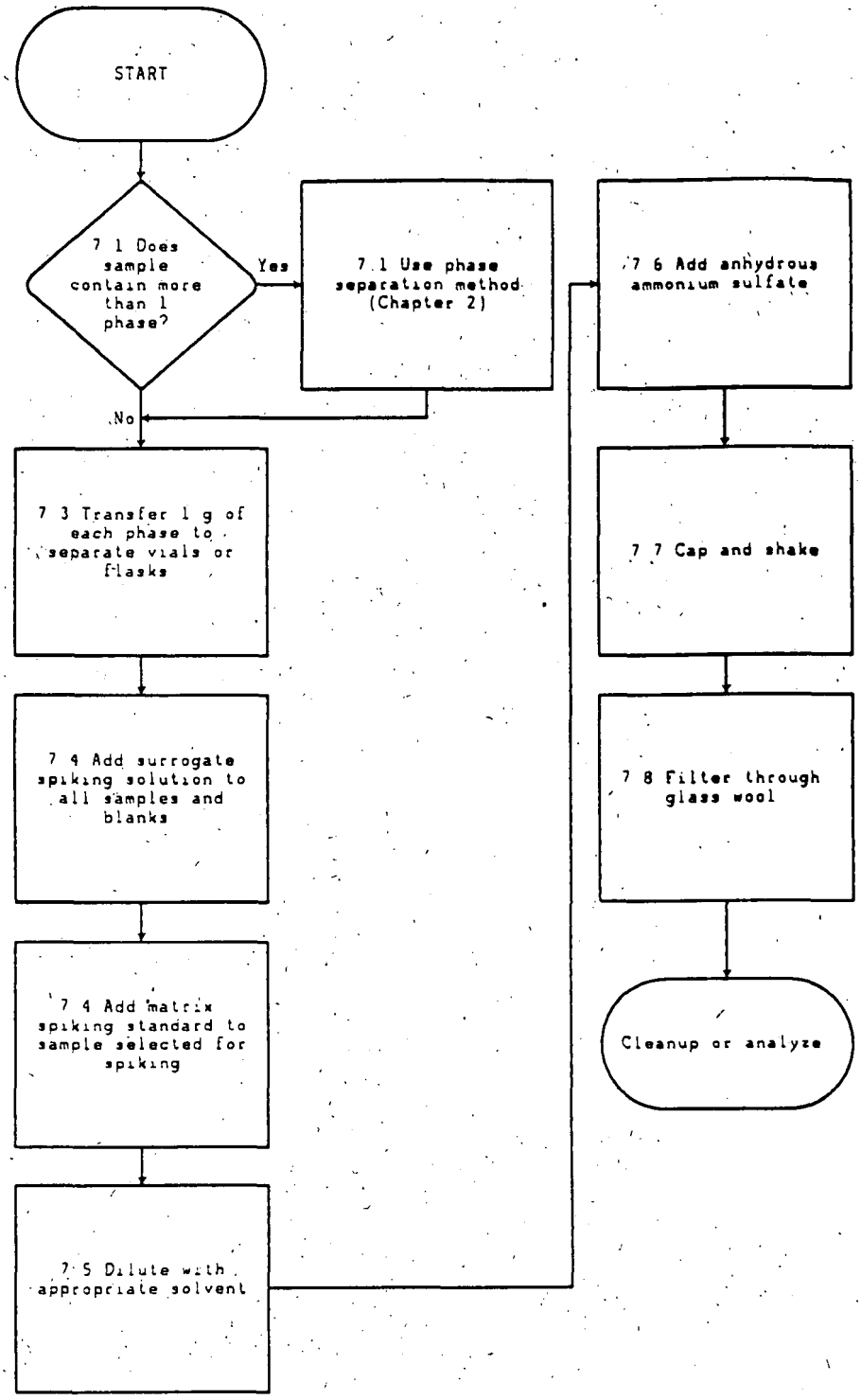
9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

10.1 None applicable.

METHOD 3580A
WASTE DILUTION



METHOD 3600A

CLEANUP

1.0 SCOPE AND APPLICATION

1.1 General

1.1.1 Injection of sample extracts, without further cleanup or isolation of analytes, into a gas or liquid chromatograph can cause extraneous peaks, deterioration of peak resolution and column efficiency, and loss of detector sensitivity and can greatly shorten the lifetime of expensive columns. The following techniques have been applied to extract purification: partitioning between immiscible solvents; adsorption chromatography; gel permeation chromatography; chemical destruction of interfering substances with acid, alkali, or oxidizing agents; and distillation. These techniques may be used individually or in various combinations, depending on the extent and nature of the co-extractives.

1.1.2 It is an unusual situation (e.g. with some water samples) when extracts can be directly determined without further treatment. Soil and waste extracts often require a combination of cleanup methods. For example, when analyzing for organochlorine pesticides and PCBs, it may be necessary to use gel permeation chromatography (GPC), to eliminate the high boiling material and a micro alumina or Florisil column to eliminate interferences with the analyte peaks on the GC/ECD.

1.2 Specific

1.2.1 Adsorption column chromatography - Alumina (Methods 3610 and 3611), Florisil (Method 3620), and silica gel (Method 3630) are useful for separating analytes of a relatively narrow polarity range away from extraneous, interfering peaks of a different polarity.

1.2.2 Acid-base partitioning (Method 3650) - Useful for separating acidic or basic organics from neutral organics. It has been applied to analytes such as the chlorophenoxy herbicides and phenols.

1.2.3 Gel permeation chromatography (GPC) (Method 3640) - The most universal cleanup technique for a broad range of semivolatile organics and pesticides. It is capable of separating high molecular-weight material from the sample analytes. It has been used successfully for all the semivolatile base, neutral, and acid compounds associated with the EPA Priority Pollutant and the Superfund Target Compound list for GC/MS analysis for semivolatiles and pesticides. GPC is usually not applicable for eliminating extraneous peaks on a chromatogram which interfere with the analytes of interest.

1.2.4 Sulfur cleanup (Method 3660) - Useful in eliminating sulfur from sample extracts, which may cause chromatographic interference with analytes of interest.

1.2.5 Table 1 indicates the recommended cleanup techniques for the indicated groups of compounds. This information can also be used as guidance for compounds that are not listed. Compounds that are chemically similar to these groups of compounds should follow a similar elution pattern.

2.0 SUMMARY OF METHOD

2.1 Refer to the specific cleanup method for a summary of the procedure.

3.0 INTERFERENCES

3.1 Analytical interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free of interferences, under the conditions of the analysis, by running laboratory reagent blanks.

3.2 More extensive procedures than those outlined in the methods may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific cleanup method for apparatus and materials needed.

5.0 REAGENTS

5.1 Refer to the specific cleanup method for the reagents needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Prior to using the cleanup procedures, samples should undergo solvent extraction. Chapter Two, Section 2.3.3, may be used as a guide for choosing the appropriate extraction procedure based on the physical composition of the waste and on the analytes of interest in the matrix (see also Method 3500 for a general description of the extraction technique). For some organic liquids, extraction prior to cleanup may not be necessary.

7.2 In most cases, the extracted sample is then analyzed by one of the determinative methods available in Section 4.3 of this chapter. If the analytes of interest are not able to be determined due to interferences, cleanup is performed.

7.3 Many of the determinative methods specify cleanup methods that should be used when determining particular analytes (e.g. Method 8060, gas chromatography of phthalate esters, recommends using either Method 3610 (Alumina column cleanup) or Method 3620 (Florisil column cleanup) if interferences prevent analysis). However, the experience of the analyst may prove invaluable in determining which cleanup methods are needed. As indicated in Section 1.0 of this method, many matrices may require a combination of cleanup procedures in order to ensure proper analytical determinations.

7.4 Guidance for cleanup is specified in each of the methods that follow. The amount of extract cleanup required prior to the final determination depends on the selectivity of both the extraction procedure and the determinative method and the required detection limit.

7.5 Following cleanup, the sample is concentrated to whatever volume is required in the determinative method. Analysis follows as specified in the determinative procedure (Section 4.3 of this Chapter).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 The analyst must demonstrate that the compounds of interest are being quantitatively recovered by the cleanup technique before the cleanup is applied to actual samples.

8.3 For sample extracts that are cleaned up, the associated quality control samples (e.g. spikes, blanks, replicates, and duplicates) must also be processed through the same cleanup procedure.

8.4 The analysis using each determinative method (GC, GC/MS, HPLC) specifies instrument calibration procedures using stock standards. It is recommended that cleanup also be performed on a series of the same type of standards to validate chromatographic elution patterns for the compounds of interest and to verify the absence of interferences from reagents.

9.0 METHOD PERFORMANCE

9.1 Refer to the specific cleanup method for performance data.

10.0 REFERENCES

10.1 Refer to the specific cleanup method.

TABLE 1.
RECOMMENDED CLEANUP TECHNIQUES FOR INDICATED GROUPS OF COMPOUNDS

Analyte Group	Determinative[a] Method	Cleanup Method Option
Phenols	8040	3630[b], 3640, 3650, 8040[c]
Phthalate esters	8060	3610, 3620, 3640
Nitrosamines	8070	3610, 3620, 3640
Organochlorine pesticides & PCBs	8080	3620, 3640, 3660
Nitroaromatics and cyclic ketones	8090	3620, 3640
Polynuclear aromatic hydrocarbons	8100	3611, 3630, 3640
Chlorinated hydrocarbons	8120	3620, 3640
Organophosphorus pesticides	8140	3620
Chlorinated herbicides	8150	8150[d]
Priority pollutant semivolatiles	8250, 8270	3640, 3650, 3660
Petroleum waste	8250, 8270	3611, 3650

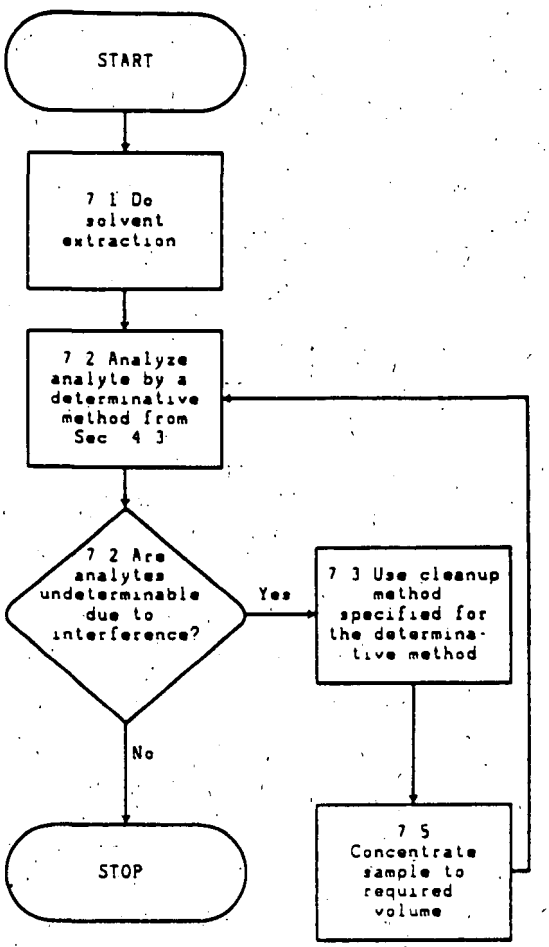
[a] The GC/MS Methods, 8250 and 8270, are also appropriate determinative methods for all analyte groups, unless lower detection limits are required.

[b] Cleanup applicable to derivatized phenols.

[c] Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered using GC/FID.

[d] Method 8150 incorporates an acid-base cleanup step as an integral part of the method.

METHOD 3600A
CLEANUP



3600B

METHOD 3600B

CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Method 3600 provides general guidance on selection of cleanup methods that are appropriate for the target analytes of interest. Cleanup methods are applied to the extracts prepared by one of the extraction methods, to eliminate sample interferences. The following table lists the cleanup methods and provides a brief description of the type of cleanup.

SW-846 CLEANUP METHODS

Method #	Method Name	Cleanup Type
3610	Alumina Cleanup	Adsorption
3611	Alumina Cleanup & Separation for Petroleum Waste	Adsorption
3620	Florisil Cleanup	Adsorption
3630	Silica Gel Cleanup	Adsorption
3640	Gel-Permeation Cleanup	Size-Separation
3650	Acid-Base Partition Cleanup	Acid-Base Partitioning
3660	Sulfur Cleanup	Oxidation/Reduction
3665	Sulfuric Acid/Permanganate Cleanup	Oxidation/Reduction

1.2 The purpose of applying a cleanup method to an extract is to remove interferences and high boiling material that may result in: (1) errors in quantitation (data may be biased low because of analyte adsorption in the injection port or front of the GC column or biased high because of overlap with an interference peak); (2) false positives because of interference peaks falling within the analyte retention time window; (3) false negatives caused by shifting the analyte outside the retention time window; (4) rapid deterioration of expensive capillary columns; and, (5) instrument downtime caused by cleaning and rebuilding of detectors and ion sources. Most extracts of soil and waste require some degree of cleanup, whereas, cleanup for water extracts may be unnecessary. Highly contaminated extracts (e.g. sample extracts of oily waste or soil containing oily residue) often require a combination of cleanup methods. For example, when analyzing for organochlorine pesticides and PCBs, it may be necessary to use gel permeation chromatography (GPC), to eliminate the high boiling material and a micro alumina or Florisil column to eliminate interferences with the analyte peaks on the GC/ECD.

1.3 The following techniques have been applied to extract purification: adsorption chromatography; partitioning between immiscible solvents; gel permeation chromatography; oxidation of interfering substances with acid, alkali, or oxidizing agents. These techniques may be used individually or in various combinations, depending on the extent and nature of the co-extractives.

1.3.1 Adsorption column chromatography - Alumina (Methods 3610 and 3611), Florisil (Method 3620), and silica gel (Method 3630) are useful for separating analytes of a relatively narrow polarity range away from extraneous, interfering peaks of a different polarity. These are primarily used for cleanup of a specific chemical group of relatively non-polar analytes, i.e., organochlorine pesticides, polynuclear aromatic hydrocarbons (PAHs), nitrosamines, etc.. Solid phase extraction cartridges have been added as an option.

1.3.2 Acid-base partitioning (Method 3650) - Useful for separating acidic or basic organics from neutral organics. It has been applied to analytes such as the chlorophenoxy herbicides and phenols. It is very useful for separating the neutral PAHs from the acidic phenols when analyzing a site contaminated with creosote and pentachlorophenol.

1.3.3 Gel permeation chromatography (GPC) (Method 3640) - The most universal cleanup technique for a broad range of semivolatile organics and pesticides. It is capable of separating high molecular-weight, high boiling material from the sample analytes. It has been used successfully for all the semivolatile base, neutral, and acid compounds associated with the EPA Priority Pollutant and the Superfund Target Compound list prior to GC/MS analysis for semivolatiles and pesticides. GPC may not be applicable to elimination of extraneous peaks on a chromatogram which interfere with the analytes of interest. It is, however, useful for the removal of high boiling materials which would contaminate injection ports and column heads, prolonging column life, stabilizing the instrument, and reducing column reactivity.

1.3.4 Sulfur cleanup (Method 3660) - Useful in eliminating sulfur from sample extracts, which may cause chromatographic interference with analytes of interest.

1.4 Several of the methods are also useful for fractionation of complex mixtures of analytes. Use the solid phase extraction cartridges in Method 3630 (Silica Gel) for separating the PCBs away from most organochlorine pesticides. Method 3611 (Alumina) is for the fractionation of aliphatic, aromatic and polar analytes. Method 3620 (Florisil) provides fractionation of the organochlorine pesticides.

1.5 Cleanup capacity is another factor that must be considered in choosing a cleanup technique. The adsorption methods (3610, 3620, and 3630) provide the option of using standard column chromatography techniques or solid phase extraction cartridges. The decision process in selecting between the different options available generally depends on the amount of interferences/high boiling material in the sample extract and the degree of cleanup required by the determinative method. The solid phase extraction cartridges require less elution solvent and less time, however, their cleanup capacity is drastically reduced when comparing a 0.5 g or 1.0 g Florisil cartridge to a 20 g standard Florisil

column. The same factor enters into the choice of the 70 g gel permeation column specified in Method 3640 versus a high efficiency column.

1.6 Table 1 indicates the recommended cleanup techniques for the indicated groups of compounds. This information can also be used as guidance for compounds that are not listed. Compounds that are chemically similar to these groups of compounds should behave similarly when taken through the cleanup procedure,however, this must be demonstrated by determining recovery of standards taken through the method.

2.0 SUMMARY OF METHOD

2.1 Refer to the specific cleanup method for a summary of the procedure.

3.0 INTERFERENCES

3.1 Analytical interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free of interferences, under the conditions of the analysis, by running laboratory reagent blanks.

3.2 More extensive procedures than those outlined in the methods may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific cleanup method for apparatus and materials needed.

5.0 REAGENTS

5.1 Refer to the specific cleanup method for the reagents needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Prior to using the cleanup procedures, samples normally undergo solvent extraction. Chapter Two, Section 2.0, may be used as a guide for choosing the appropriate extraction procedure based on the physical composition of the waste and on the analytes of interest in the matrix (see also Method 3500 for a general description of the extraction technique). For some organic liquids, extraction prior to cleanup may not be necessary.

7.2 Most soil/sediment and waste sample extracts will require some degree of cleanup. The extract is then analyzed by one of the determinative methods. If interferences still preclude analysis for the analytes of interest, additional cleanup may be required.

7.3 Many of the determinative methods specify cleanup methods that should be used when determining particular analytes (e.g. Method 8061, gas chromatography of phthalate esters, recommends using either Method 3610 (Alumina column cleanup) or Method 3620 (Florisil column cleanup) if interferences prevent analysis. However, the experience of the analyst may prove invaluable in determining which cleanup methods are needed. As indicated in Section 1.0 of this method, many matrices may require a combination of cleanup procedures in order to ensure proper analytical determinations.

7.4 Guidance for cleanup is specified in each of the methods that follow. The amount of extract cleanup required prior to the final determination depends on the concentration of interferences in the sample, the selectivity of both the extraction procedure and the determinative method and the required detection limit.

7.5 Following cleanup, the sample is concentrated to whatever volume is required in the determinative method. Analysis follows as specified in the determinative procedure.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 The analyst must demonstrate that the compounds of interest are being quantitatively recovered by the cleanup technique before the cleanup is applied to actual samples. For sample extracts that are cleaned up, the associated quality control samples (e.g. spikes, blanks, replicates, and duplicates) must also be processed through the same cleanup procedure.

8.3 The analysis using each determinative method (GC, GC/MS, HPLC) specifies instrument calibration procedures using stock standards. It is recommended that cleanup also be performed on a series of the same type of standards to validate chromatographic elution patterns for the compounds of interest and to verify the absence of interferences from reagents.

9.0 METHOD PERFORMANCE

9.1 Refer to the specific cleanup method for performance data.

10.0 REFERENCES

10.1 Refer to the specific cleanup method.

TABLE 1.
RECOMMENDED CLEANUP TECHNIQUES FOR INDICATED GROUPS OF COMPOUNDS

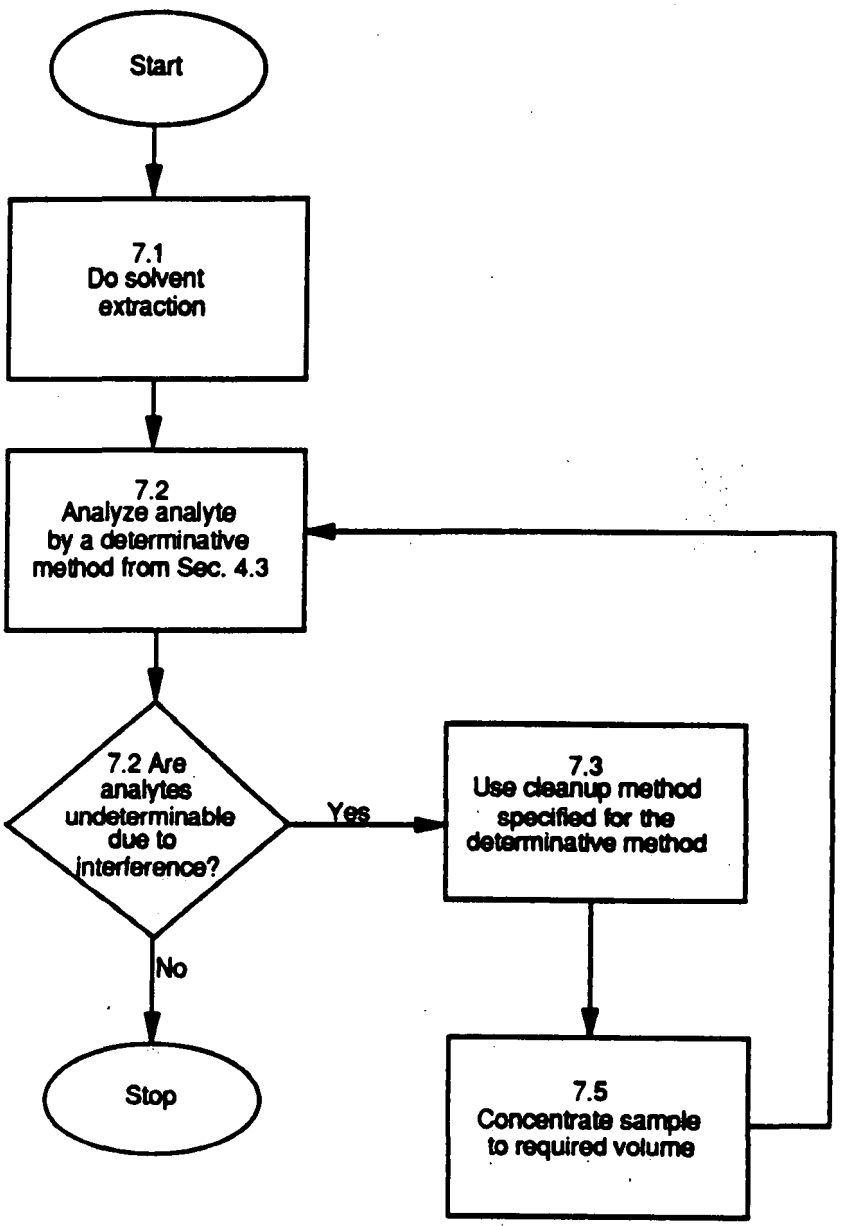
Analyte Group	Determinative[a] Method	Cleanup Method Options
Phenols	8040	3630[b], 3640, 3650, 8040[c]
Phthalate esters	8060/8061	3610, 3620, 3640
Nitrosamines	8070	3610, 3620, 3640
Organochlorine pesticides & PCBs	8080/8081	3620, 3640, 3660
PCBs	8080/8081	3665
Nitroaromatics and cyclic ketones	8090	3620, 3640
Polynuclear aromatic hydrocarbons	8100/8310	3611, 3630, 3640
Chlorinated hydrocarbons	8120/8121	3620, 3640
Organophosphorus pesticides	8140/8141	3620
Chlorinated herbicides	8150/8151	8150[d], 8151[d], 3620
Semivolatile organics	8250/8270	3640, 3650, 3660
Petroleum waste	8250/8270	3611, 3650
PCDDs and PCDFs by LR/MS	8280	8280
PCDDs and PCDFs by HR/MS	8290	8290
N-methyl carbamate pesticides	8318	8318

[a] The GC/MS Methods, 8250 and 8270, are also appropriate determinative methods for all analyte groups, unless lower detection limits are required.

[b] Cleanup applicable to derivatized phenols.

[c] Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered using GC/FID.

[d] Methods 8150 and 8151 incorporate an acid-base cleanup step as an integral part of the methods.


Start
7.1
Do solvent
extraction
7.2
Analyze analyte
by a determinative
method from Sec. 4.3
7.2 Are
analytes
undeterminable
due to
interference?
Yes
No
7.3
Use cleanup method
specified for the
determinative method
Stop
7.5
Concentrate sample
to required volume

METHOD 3610A

ALUMINA COLUMN CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Scope: Alumina is a highly porous and granular form of aluminum oxide. It is available in three pH ranges (basic, neutral, and acidic) for use in column chromatography. It is used to separate analytes from interfering compounds of a different chemical polarity.

1.2 General Applications (Gordon and Ford):

1.2.1 **Basic** (B) pH (9-10): USES: Basic and neutral compounds stable to alkali, alcohols, hydrocarbons, steroids, alkaloids, natural pigments. DISADVANTAGES: Can cause polymerization, condensation, and dehydration reactions; cannot use acetone or ethyl acetate as eluants.

1.2.2 **Neutral** (N): USES: Aldehydes, ketones, quinones, esters, lactones, glycoside. DISADVANTAGES: Considerably less active than the basic form.

1.2.3 **Acidic** (A) pH (4-5): USES: Acidic pigments (natural and synthetic), strong acids (that otherwise chemisorb to neutral and basic alumina).

1.2.4 **Activity grades**: Acidic, basic, or neutral alumina can be prepared in various activity grades (I to V), according to the Brockmann scale, by addition of water to Grade 1 (prepared by heating at 400-450°C until no more water is lost). The Brockmann scale (Gordon and Ford, p. 374) is reproduced below:

Water added (wt. %):	0	3	6	10	15
Activity grade:	I	II	III	IV	V
RF (p-aminoazobenzene):	0.0	0.13	0.25	0.45	0.55

1.3 Specific applications: This method includes guidance for cleanup of sample extracts containing phthalate esters and nitrosamines. For alumina column cleanup of petroleum wastes, see Method 3611, Alumina Column Cleanup of Petroleum Wastes.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required amount of adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution of the analytes is effected with a suitable solvent(s), leaving the interfering compounds on the column. The eluate is then concentrated (if necessary).

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Chromatography column: 300 mm x 10 mm ID, with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Beakers: 500 mL.

4.3 Reagent bottle: 500 mL.

4.4 Muffle furnace.

4.5 Kuderna-Danish (K-D) apparatus:

4.5.1 Concentrator tube: 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.5.2 Evaporation flask: 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.5.3 Snyder column: Three ball macro (Kontes K-503000-0121 or equivalent).

4.5.4 Snyder column: Two ball micro (Kontes K-569001-0219 or equivalent).

4.5.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.6 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.7 Water bath: Heated, with concentric ring cover, capable of temperature control ($\pm 5^{\circ}C$). The bath should be used in a hood.

4.8 Vials: Glass, 2 mL capacity, with Teflon lined screw caps or crimp tops.

4.9 Erlenmeyer flasks: 50 and 250 mL

5.0 REAGENTS

5.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Sodium sulfate: Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.3 Eluting solvents:

5.3.1 Diethyl Ether, $C_2H_5OC_2H_5$. Pesticide quality or equivalent. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

5.3.2 Methanol, CH_3OH - Pesticide quality or equivalent.

5.3.3 Pentane, $CH_3(CH_2)_3CH_3$ - Pesticide quality or equivalent.

5.3.4 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.3.5 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.4 <u>Alumina</u>:

5.4.1 For cleanup of phthalate extracts: Alumina-Neutral, activity Super I, W200 series (ICN Life Sciences Group, No. 404583, or equivalent). To prepare for use, place 100 g of alumina into a 500 mL beaker and heat for approximately 16 hr at 400°C. After heating, transfer to a 500 mL reagent bottle. Tightly seal and cool to room temperature. When cool, add 3 mL of organic-free reagent water. Mix thoroughly by shaking or rolling for 10 min and let it stand for at least 2 hr. Keep the bottle sealed tightly.

5.4.2 For cleanup of nitrosamine extracts: Alumina-Basic, activity Super I, W200 series (ICN Life Sciences Group, No. 404571, or equivalent). To prepare for use, place 100 g of alumina into a 500 mL reagent bottle and add 2 mL of organic-free reagent water. Mix the alumina preparation thoroughly by shaking or rolling for 10 min and let it stand for at least 2 hr. The preparation should be homogeneous before use. Keep the bottle sealed tightly to ensure proper activity.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Phthalate esters:

7.1.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.1.2 Place approximately 10 g of alumina into a 10 mm ID chromatographic column. Tap the column to settle the alumina and add 1-2 cm of anhydrous sodium sulfate to the top.

7.1.3 Pre-elute the column with 40 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2 mL sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 35 mL of hexane and continue the elution of the column. Discard this hexane eluate.

7.1.4 Next, elute the column with 140 mL of 20% ethyl ether in hexane (v/v) into a 500 mL K-D flask equipped with a 10 mL concentrator tube. Concentrate the collected fraction using the Kuderna-Danish technique. No solvent exchange is necessary. Adjust the volume of the cleaned up extract to whatever volume is required (10.0 mL for Method 8060) and analyze. Compounds that elute in this fraction are as follows:

Bis(2-ethylhexyl) phthalate
Butyl benzyl phthalate
Di-n-butyl phthalate
Diethyl phthalate
Dimethyl phthalate
Di-n-octyl phthalate.

7.2 Nitrosamines:

7.2.1 Reduce the sample extract to 2 mL prior to cleanup.

7.2.2 Diphenylamine, if present in the original sample extract, must be separated from the nitrosamines if N-nitrosodiphenylamine is to be determined by this method.

7.2.3 Place approximately 12 g of the alumina preparation into a 10 mm ID chromatographic column. Tap the column to settle the alumina and add 1-2 cm of anhydrous sodium sulfate to the top.

7.2.4 Pre-elute the column with 10 mL of ethyl ether/pentane (3:7)(v/v). Discard the eluate (about 2 mL) and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2 mL sample extract onto the column using an additional 2 mL of pentane to complete the transfer.

7.2.5 Just prior to exposure of the sodium sulfate layer to the air, add 70 mL of ethyl ether/pentane (3:7)(v/v). Discard the first 10 mL of eluate. Collect the remainder of the eluate in a 500 mL K-D flask

equipped with a 10 mL concentrator tube. This fraction contains N-nitroso-di-n-propylamine.

7.2.6 Next, elute the column with 60 mL of ethyl ether/pentane (1:1)(v/v), collecting the eluate in a second 500 mL K-D flask equipped with a 10 mL concentrator tube. Add 15 mL of methanol to the K-D flask. This fraction will contain N-nitrosodimethylamine, most of the N-nitroso-di-n-propylamine, and any diphenylamine that is present.

7.2.7 Concentrate both fractions using the Kuderna-Danish Technique (if necessary), using pentane to prewet the Snyder column. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of pentane. Adjust the final volume to whatever is required in the appropriate determinative method (Section 4.3 of this chapter). Analyze the fractions.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

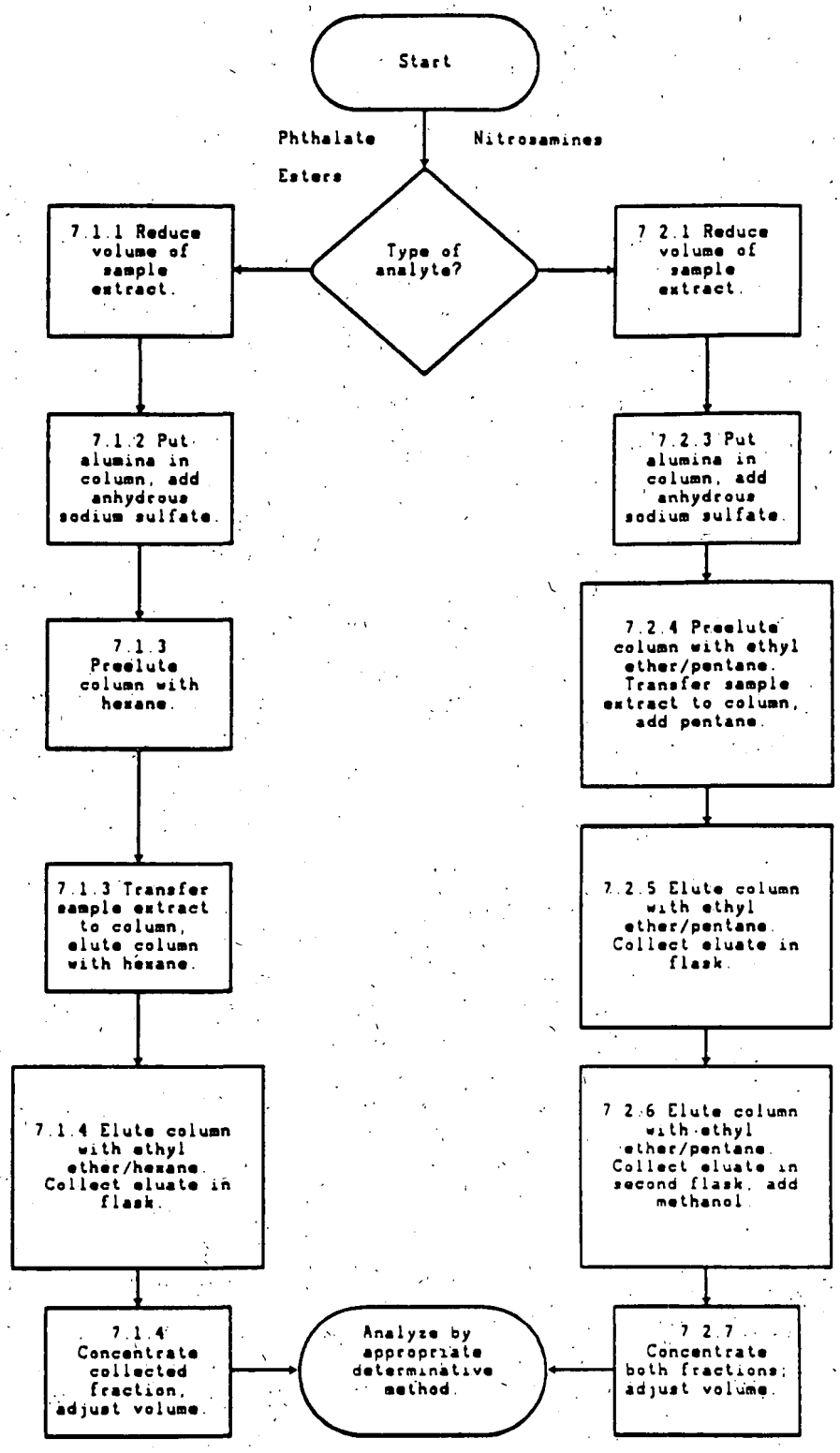
9.0 METHOD PERFORMANCE

9.1 Performance data are not available.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

METHOD 3610A
ALUMINA COLUMN CLEANUP



METHOD 3611A

ALUMINA COLUMN CLEANUP AND SEPARATION OF PETROLEUM WASTES

1.0 SCOPE AND APPLICATION

1.1 Method 3611 was formerly Method 3570 in the Second Edition of this manual.

1.2 Specific application: This method includes guidance for separation of petroleum wastes into aliphatic, aromatic, and polar fractions.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required amount of adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution of the analytes is effected with a suitable solvent(s), leaving the interfering compounds on the column. The eluate is then concentrated (if necessary).

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.3 Caution must be taken to prevent overloading of the chromatographic column. As the column loading for any of these types of wastes approaches 0.300 g of extractable organics, separation recoveries will suffer. If overloading is suspected, an aliquot of the base-neutral extract prior to cleanup may be weighed and then evaporated to dryness. A gravimetric determination on the aliquot will indicate the weight of extractable organics in the sample.

3.4 Mixtures of petroleum wastes containing predominantly polar solvents, i.e., chlorinated solvents or oxygenated solvents, are not appropriate for this method.

4.0 APPARATUS AND MATERIALS

4.1 Chromatography column: 300 mm x 10 mm ID, with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Beakers: 500 mL.

4.3 Reagent bottle: 500 mL.

4.4 Muffle furnace.

4.5 Kuderna-Danish (K-D) apparatus:

4.5.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.5.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.5.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.5.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.5.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.6 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.7 Water bath: Heated with concentric ring cover, capable of temperature control ($\pm 5^{\circ}C$). The bath should be used in a hood.

4.8 Erlenmeyer flasks: 50 and 250 mL.

5.0 REAGENTS

5.1 Sodium sulfate: (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.2 Eluting solvents:

5.2.1 Methanol, CH_3OH - Pesticide quality or equivalent.

5.2.2 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.2.3 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.3 Alumina: Neutral 80-325 MCB chromatographic grade or equivalent. Dry alumina overnight at 130°C prior to use.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 It is suggested that Method 3650, Acid-Base Partition Cleanup, be performed on the sample extract prior to alumina cleanup.

7.2 Place approximately 10 g of alumina into a chromatographic column, tap to settle the alumina, and add 1 cm of anhydrous sodium sulfate to the top.

7.3 Pre-elute the column with 50 mL of hexane. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 1 mL sample extract onto the column using an additional 1 mL of hexane to complete the transfer. To avoid overloading the column, it is suggested that no more than 0.300 g of extractable organics be placed on the column (see Section 3.3).

7.4 Just prior to exposure of the sodium sulfate to the air, elute the column with a total of 15 mL of hexane. If the extract is in 1 mL of hexane, and if 1 mL of hexane was used as a rinse, then 13 mL of additional hexane should be used. Collect the effluent in a 50 mL flask and label this fraction "base/neutral aliphatics." Adjust the flow rate to 2 mL/min.

7.5 Elute the column with 100 mL of methylene chloride and collect the effluent in a 250 mL flask. Label this fraction "base/neutral aromatics."

7.6 Elute the column with 100 mL of methanol and collect the effluent in a 250 mL flask. Label this fraction "base/neutral polars."

7.7 Concentrate the extracts (if necessary) by the standard K-D technique to the volume (1-10 mL) required in the appropriate determinative method (Chapter Four). Analyze the fractions containing the analytes of interest.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.

9.2 Rag oil is an emulsion consisting of crude oil, water, and soil particles. It has a density greater than crude oil and less than water. This material forms a layer between the crude oil and water when the crude oil is allowed to gravity separate at the refinery. A rag oil sample was analyzed by a number of laboratories according to the procedure outlined in this method. The results of these analyses by GC/MS for selected components in the rag oil are presented in Table 1. Reconstructed ion chromatograms from the GC/MS analyses are included as Figures 1 and 2.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

Table 1.
RESULTS OF ANALYSIS FOR SELECTED COMPONENTS IN RAG OIL

Analyte	Mean Conc. (mg/kg)[a]	Standard Deviation	%RSD[b]
Naphthalene	216	42	19
Fluorene	140	66	47
Phenanthrene	614	296	18
2-Methylnaphthalene	673	120	18
Dibenzothiophene	1084	286	26
Methylphenanthrene	2908	2014	69
Methyldibenzothiophene	2200	1017	46
	Average Surrogate Recovery		
Nitrobenzene-d_5	58.6	11	
Terphenyl-d_{14}	83.0	2.6	
Phenol-d_6	80.5	27.6	
Naphthalene-d_8	64.5	5.0	

[a] Based on five determinations from three laboratories.

[b] Percent Relative Standard Deviation.

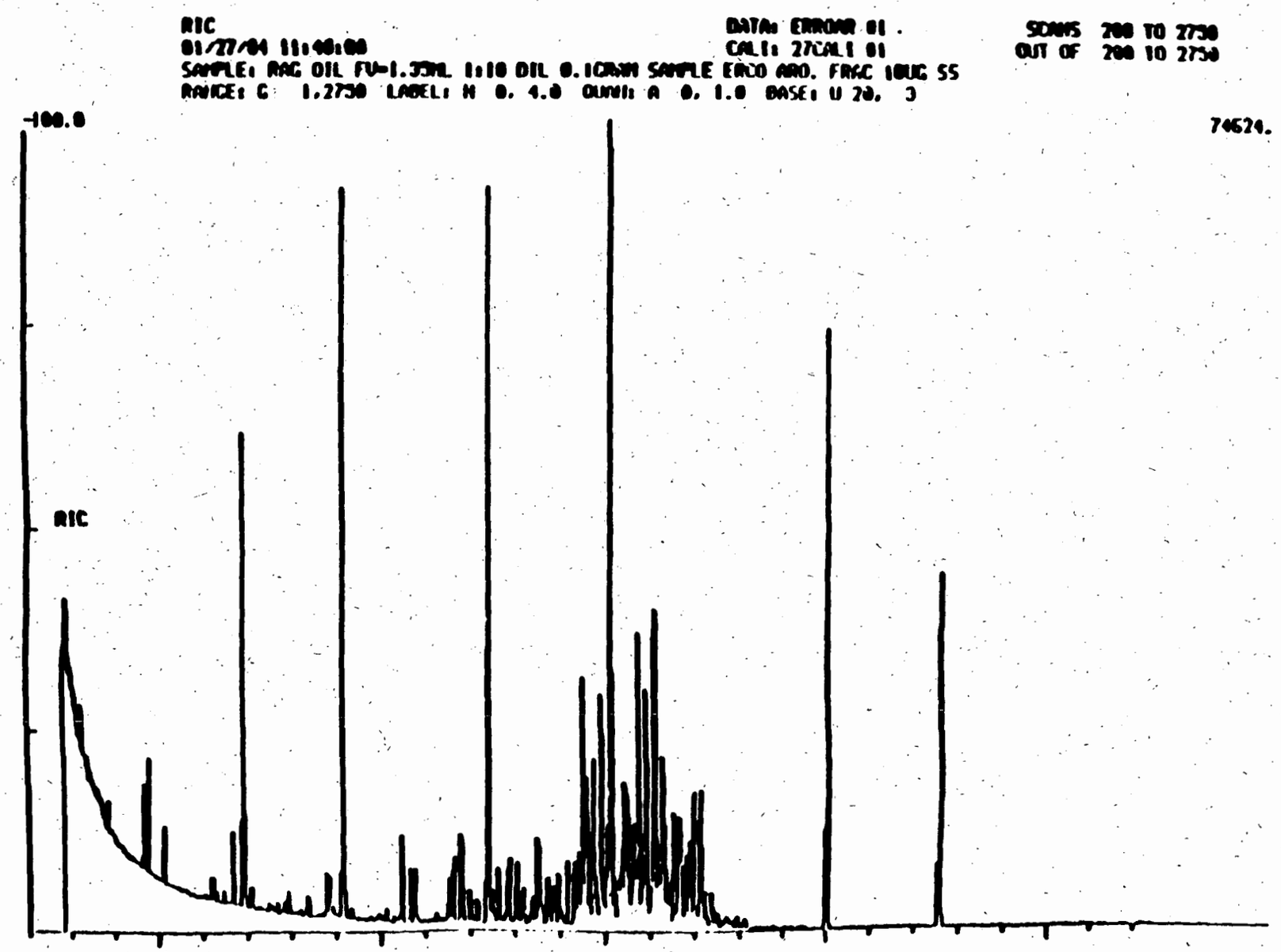


Figure 1. Reconstructed ion chromatogram from GC/MS analysis of the aromatic fraction from Rag Oil

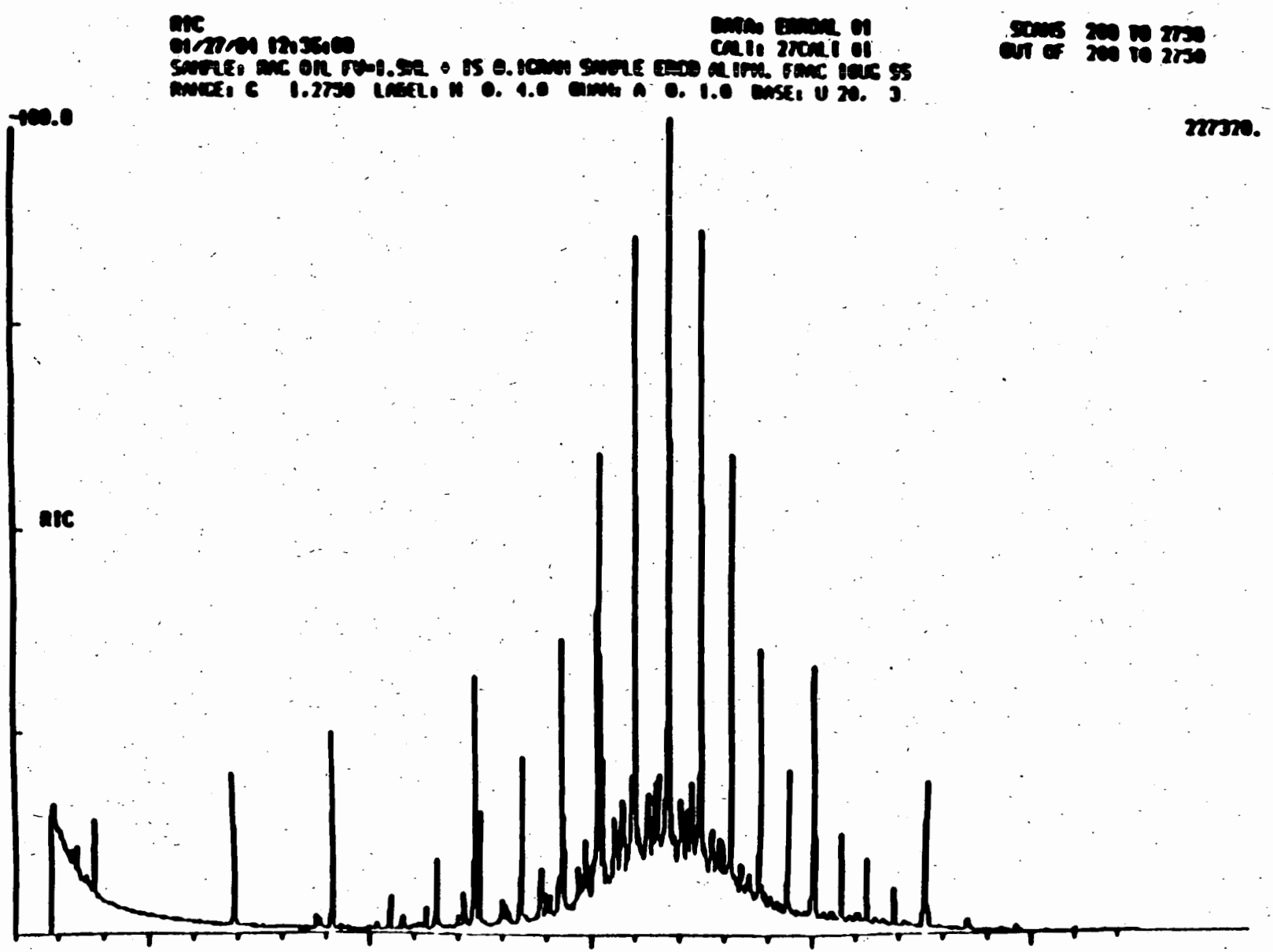
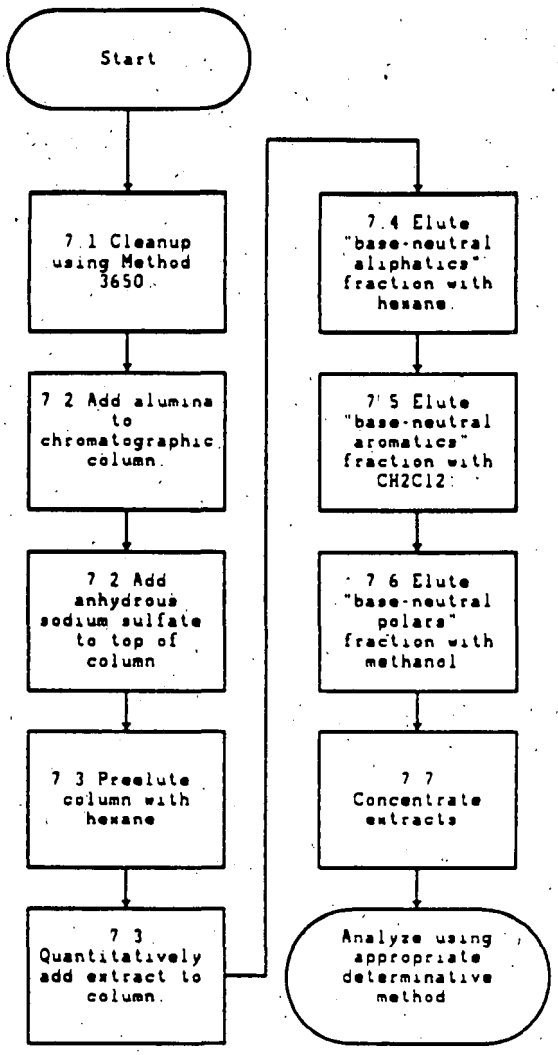


Figure 2. Reconstructed ion chromatogram from GC/MS analysis of the aliphatic fraction from Rag Oil


Start
7.1 Cleanup using Method 3650.
7.2 Add alumina to chromatographic column.
7.2 Add anhydrous sodium sulfate to top of column
7.3 Preelute column with hexane
7.3 Quantitatively add extract to column.
7.4 Elute "base-neutral aliphatics" fraction with hexane.
7.5 Elute "base-neutral aromatics" fraction with CH2Cl2
7.6 Elute "base-neutral polars" fraction with methanol
7.7 Concentrate extracts
Analyze using appropriate determinative method

METHOD 3620A

FLORISIL COLUMN CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Florisil, a registered trade name of the Floridin Co., is a magnesium silicate with acidic properties. It is used for general column chromatography as a cleanup procedure prior to sample analysis by gas chromatography.

1.2 General applications: Cleanup of pesticide residues and other chlorinated hydrocarbons; the separation of nitrogen compounds from hydrocarbons; the separation of aromatic compounds from aliphatic-aromatic mixtures; and similar applications for use with fats, oils, and waxes (Floridin). Additionally, Florisil is considered good for separations with steroids, esters, ketones, glycerides, alkaloids, and some carbohydrates (Gordon and Ford).

1.3 Specific applications: This method includes guidance for cleanup of sample extracts containing the following analyte groups: phthalate esters; nitrosamines; organochlorine pesticides; nitroaromatics; haloethers; chlorinated hydrocarbons; and organophosphorus pesticides.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution is effected with a suitable solvent(s) leaving the interfering compounds on the column. The eluate is then concentrated (if necessary).

3.0 INTERFERENCES

3.1 A reagent blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Beaker - 500 mL.

4.2 Chromatographic column - 300 mm long x 10 mm ID or 400 mm long x 20 mm ID, as specified in Section 7.0; with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of

acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus.

4.3.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.4 Muffle furnace.

4.5 Reagent bottle - 500 mL.

4.6 Water bath - Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.7 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.8 Erlenmeyer flasks - 50 and 250 mL.

4.9 Top-loading balance - 0.01 g.

5.0 REAGENTS

5.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Florisil - Pesticide residue (PR) grade (60/100 mesh); purchase activated at 1250°F (677°C), stored in glass containers with ground-glass stoppers or foil-lined screw caps.

5.2.1 Deactivation of Florisil - for cleanup of phthalate esters. To prepare for use, place 100 g of Florisil into a 500 mL beaker and heat for approximately 16 hr at 40°C. After heating, transfer to a 500 mL reagent bottle. Tightly seal and cool to room temperature. When cool add 3 mL of organic-free reagent water. Mix thoroughly by shaking or rolling for 10 min and let stand for at least 2 hr. Keep the bottle sealed tightly.

5.2.2 Activation of Florisil - for cleanup of nitrosamines,

organochlorine pesticides and PCBs, nitroaromatics, haloethers, chlorinated hydrocarbons, and organophosphorus pesticides. Just before use, activate each batch at least 16 hr at 130°C in a glass container loosely covered with aluminum foil. Alternatively, store the Florisil in an oven at 130°C. Cool the Florisil before use in a desiccator. (Florisil from different batches or sources may vary in adsorptive capacity. To standardize the amount of Florisil which is used, the use of lauric acid value is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per g of Florisil. The amount of Florisil to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 g (Mills).

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4 - Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Eluting solvents

5.4.1 Diethyl ether, $C_2H_5OC_2H_5$ - Pesticide quality or equivalent. Must be free of peroxides, as indicated by test strips (EM Quant or equivalent). Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL ethyl alcohol preservative must be added to each liter of ether.

5.4.2 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.4.3 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.4.4 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.4.5 Pentane, $CH_3(CH_2)_3CH_3$ - Pesticide quality or equivalent.

5.4.6 Petroleum ether (boiling range 30-60°C) - Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Phthalate esters

7.1.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.1.2 Place approximately 10 g of deactivated Florisil (Section 5.1.1) into a 10 mm ID chromatographic column. Tap the column to settle the Florisil and add approximately 1 cm of anhydrous sodium sulfate to the

top.

7.1.3 Preelute the column with 40 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2 mL sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 40 mL of hexane and continue the elution of the column. Discard this hexane eluate.

7.1.4 Next, elute the column with 100 mL of 20% ethyl ether in hexane (v/v) into a 500 mL K-D flask equipped with a 10 mL concentrator tube. Concentrate the collected fraction as needed. No solvent exchange is necessary. Adjust the volume of the cleaned-up extract to whatever volume is required (10 mL for Method 8060) and analyze by gas chromatography. Compounds that elute in this fraction are:

Bis(2-ethylhexyl) phthalate
Butyl benzyl phthalate
Di-n-butyl phthalate
Diethyl phthalate
Dimethyl phthalate
Di-n-octyl phthalate

7.2 Nitrosamines

7.2.1 Reduce the sample extract volume to 2 mL prior to cleanup.

7.2.2 Add a weight of activated Florisil (nominally 22 g) predetermined by calibration (Section 5.1.2) into a 20 mm ID chromatographic column. Tap the column to settle the Florisil and add about 5 mm of anhydrous sodium sulfate to the top.

7.2.3 Pre-elute the column with 40 mL of ethyl ether/pentane (15:85) (v/v). Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2 mL sample extract onto the column using an additional 2 mL of pentane to complete the transfer.

7.2.4 Elute the column with 90 mL of ethyl ether/pentane (15:85) (v/v) and discard the eluate. This fraction will contain the diphenylamine, if it is present in the extract.

7.2.5 Next, elute the column with 100 mL of acetone/ethyl ether (5:95) (v/v) into a 500 mL K-D flask equipped with a 10 mL concentrator tube. This fraction will contain all of the nitrosamines listed in the scope of the method.

7.2.6 Add 15 mL of methanol to the collected fraction, concentrate as needed using pentane to prewet the K-D column and set the water bath at 70 to 75°C. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of pentane.

7.3 Organochlorine pesticides, haloethers, and organophosphorus pesticides (see Tables 1 and 2 for fractionation patterns of compounds tested)

7.3.1 Reduce the sample extract volume to 10 mL prior to cleanup. The extract solvent must be hexane.

7.3.2 Add a weight of activated Florisil (nominally 20 g), predetermined by calibration (Section 5.1.2), to a 20 mm ID chromatographic column. Settle the Florisil by tapping the column. Add anhydrous sodium sulfate to the top of the Florisil to form a layer 1 to 2 cm deep. Add 60 mL of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate to air, stop the elution of the hexane by closing the stopcock on the chromatographic column. Discard the eluate.

7.3.3 Adjust the sample extract volume to 10 mL with hexane and transfer it from the K-D concentrator tube to the Florisil column. Rinse the tube twice with 1-2 mL hexane, adding each rinse to the column.

7.3.4 Place a 500 mL K-D flask and clean concentrator tube under the chromatographic column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 mL of 6% ethyl ether in hexane (v/v) (Fraction 1) using a drip rate of about 5 mL/min. All of the haloethers are in this fraction. Remove the K-D flask and set aside for later concentration. Elute the column again, using 200 mL of 15% ethyl ether in hexane (v/v) (Fraction 2), into a second K-D flask. Perform a third elution using 200 mL of 50% ethyl ether in hexane (v/v) (Fraction 3), and a final elution with 200 mL of 100% ethyl ether (Fraction 4), into separate K-D flasks.

7.3.5 If necessary, concentrate the eluates by standard K-D techniques using the water bath at about 85°C (75°C for Fraction 4). Adjust the final volume to whatever volume is required (1-10 mL).

7.4 Nitroaromatics and isophorone

7.4.1 Reduce the sample extract volume to 2 mL prior to cleanup.

7.4.2 Add a weight of activated Florisil (nominally 10 g) predetermined by calibration (Section 5.1.2) into a 10 mm ID chromatographic column. Tap the column to settle the Florisil and add about 1 cm of anhydrous sodium sulfate to the top.

7.4.3 Pre-elute the column with methylene chloride/hexane (1:9) (v/v) at about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 30 mL of methylene chloride/hexane (1:9) (v/v) and continue the elution of the column. Discard the eluate.

7.4.4 Elute the column with 90 mL of ethyl ether/pentane (15:85) (v/v) and discard the eluate. This fraction will contain the diphenylamine, if it is present in the extract.

7.4.5 Next, elute the column with 100 mL of acetone/ethyl ether (5:95) (v/v) into a 500 mL K-D flask equipped with a 10 mL concentrator tube. This fraction will contain all of the nitrosamines listed in the scope of the method.

7.4.6 Add 15 mL of methanol to the collected fraction, concentrate using pentane to prewet the K-D column, and set the water bath at 70 to 75°C. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of pentane.

7.4.7 Next, elute the column with 30 mL of acetone/methylene chloride (1:9) (v/v) into a 500 mL K-D flask equipped with a 10 mL concentrator tube. Concentrate the collected fraction, while exchanging the solvent to hexane. To exchange the solvent, reduce the elution solvent to about 10 mL. Add 50 mL of hexane, a fresh boiling chip, and return the reassembled K-D apparatus to the hot water bath. Adjust the final volume of the cleaned-up extract to whatever volume is required (1-10 mL). Compounds that elute in this fraction are:

2,4-Dinitrotoluene
2,6-Dinitrotoluene
Isophorone
Nitrobenzene.

7.5 Chlorinated hydrocarbons

7.5.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.5.2 Add a weight of activated Florisil (nominally 12 g) predetermined by calibration (Section 5.1.2) into a 10 mm ID chromatographic column. Tap the column to settle the Florisil and add about 1 to 2 cm of anhydrous sodium sulfate to the top.

7.5.3 Preelute the column with 100 mL of petroleum ether. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the sample extract to the column by decantation and subsequent petroleum ether washings. Discard the eluate. Just prior to exposure of the sodium sulfate layer to the air, begin eluting the column with 200 mL of petroleum ether and collect the eluate in a 500 mL K-D flask equipped with a 10 mL concentrator tube. This fraction should contain all of the chlorinated hydrocarbons:

2-Chloronaphthalene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
1,2,4-Trichlorobenzene.

7.5.4 Concentrate the fraction, using hexane to prewet the column. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with hexane. Adjust the final volume of the cleaned-up extract to whatever volume is required (1-10 mL).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples should also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Table 1 indicates the distribution of chlorinated pesticides, PCB's, and haloethers in various Florisil column fractions.

9.2 Table 2 indicates the distribution of organophosphorus pesticides in various Florisil column fractions.

10.0 REFERENCES

1. Gordon, A.J. and R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References (New York: John Wiley & Sons, Inc.), pp. 372, 374, and 375, 1972.

2. Floridin of ITT System, Florisil: Properties, Application, Bibliography, Pittsburgh, Pennsylvania, 5M381DW.

3. Mills, P.A., "Variation of Florisil Activity; Simple Method for Measuring Absorbent Capacity and its use in Standardizing Florisil Columns," Journal of the Association of Official Analytical Chemists, 51, 29, 1968.

4. U.S. Food and Drug Association, Pesticides Analytical Manual (Volume 1), July 1985.

5. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

TABLE 1

DISTRIBUTION OF CHLORINATED PESTICIDES, PCBs, AND HALOETHERS INTO FLORISIL COLUMN FRACTIONS

Parameter	Percent Recovery by Fraction[a]		
	1	2	3
Aldrin	100		
α-BHC	100		
β-BHC	97		
γ-BHC	98		
δ-BHC	100		
Chlordane	100		
4,4'-DDD	99		
4,4'-DDE	98		
4,4'-DDT	100		
Dieldrin	0	100	
Endosulfan I	37	64	
Endosulfan II	0	7	91
Endosulfan sulfate	0	0	106
Endrin	4	96	
Endrin aldehyde	0	68	26
Haloethers	R		
Heptachlor	100		
Heptachlor epoxide	100		
Toxaphene	96		
PCB-1016	97		
PCB-1221	97		
PCB-1232	95	4	
PCB-1242	97		
PCB-1248	103		
PCB-1254	90		
PCB-1260	95		

[a] Eluant composition: Fraction 1 - 6% ethyl ether in hexane
Fraction 2 - 15% ethyl ether in hexane
Fraction 3 - 50% ethyl ether in hexane

R = Recovered (no percent recovery data presented).

SOURCE: U.S. EPA and FDA data.

TABLE 2

DISTRIBUTION OF ORGANOPHOSPHORUS PESTICIDES INTO FLORISIL COLUMN FRACTIONS

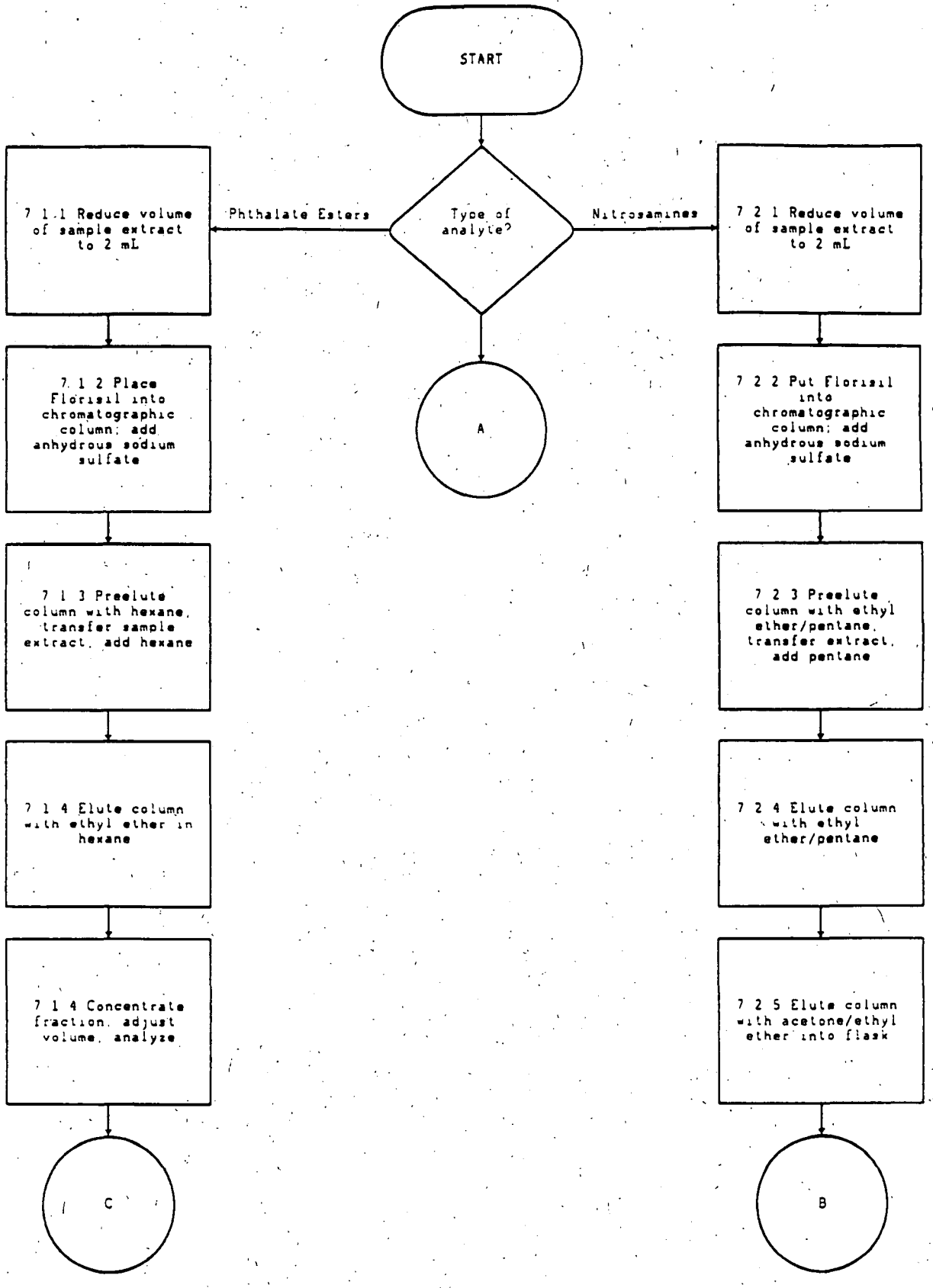
Parameter	Percent Recovery by Fraction[a]			
	1	2	3	4
Azinphos methyl			20	80
Bolstar (Sulprofos)	ND	ND	ND	ND
Chlorpyrifos	>80			
Coumaphos	NR	NR	NR	
Demeton	100			
Diazinon		100		
Dichlorvos	NR	NR	NR	
Dimethoate	ND	ND	ND	ND
Disulfoton	25-40			
EPN		>80		
Ethoprop	V	V	V	
Fensulfothion	ND	ND	ND	ND
Fenthion	R	R		
Malathion		5	95	
Merphos	V	V	V	
Mevinphos	ND	ND	ND	ND
Monochrotophos	ND	ND	ND	ND
Naled	NR	NR	NR	
Parathion		100		
Parathion methyl		100		
Phorate	0-62			
Ronnel	>80			
Stirophos (Tetrachlorvinphos)	ND	ND	ND	ND
Sulfotepp	V	V		
TEPP	ND	ND	ND	ND
Tokuthion (Prothiofos)	>80			
Trichloronate	>80			

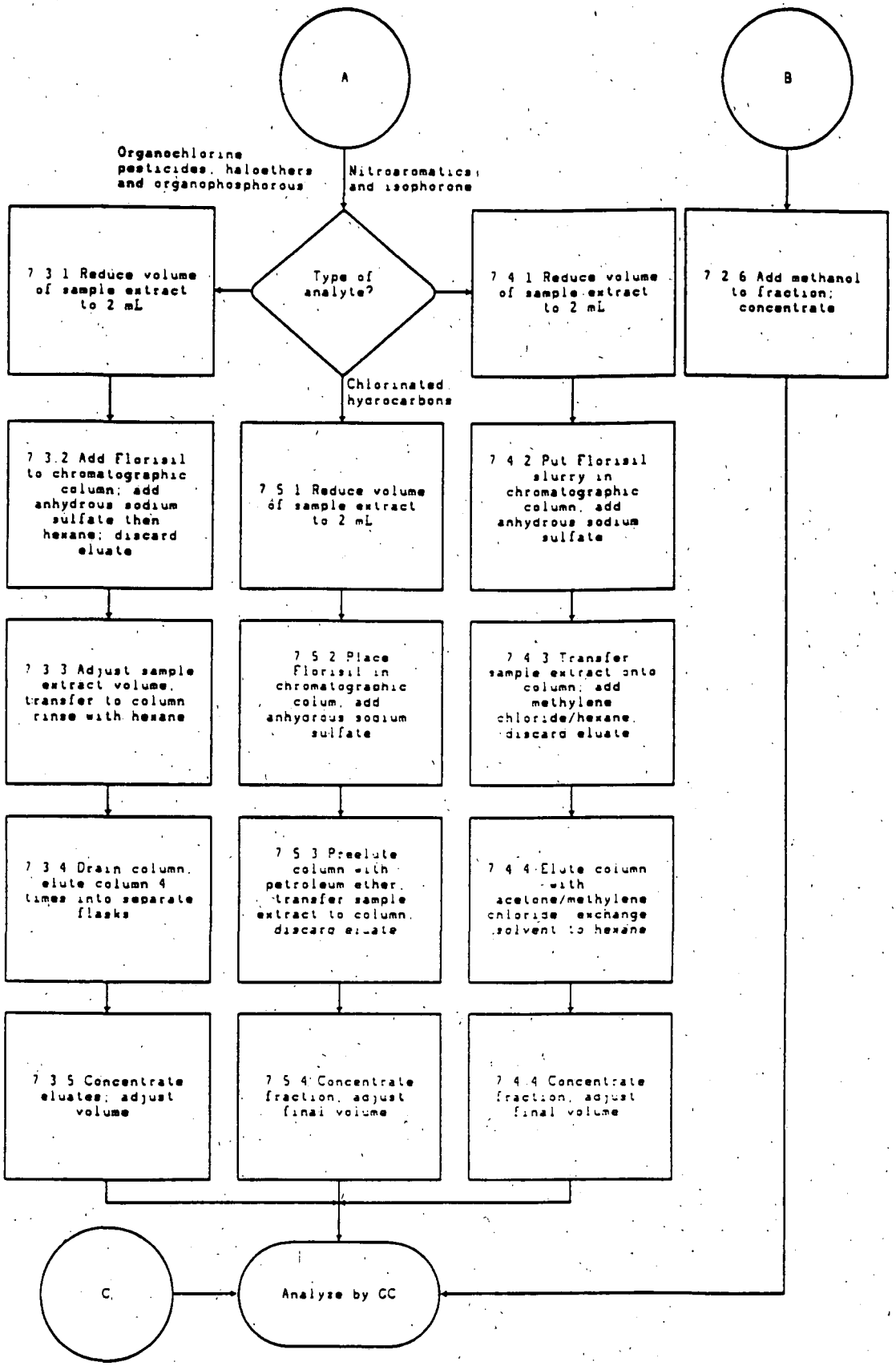
[a] Eluant composition:
Fraction 1 - 200 mL of 6% ethyl ether in hexane
Fraction 2 - 200 mL of 15% ethyl ether in hexane
Fraction 3 - 200 mL of 50% ethyl ether in hexane
Fraction 4 - 200 mL of 100% ethyl ether

R = Recovered (no percent recovery information presented) (U.S. FDA).
NR = Not recovered (U.S. FDA).
V = Variable recovery (U.S. FDA).
ND = Not determined.

SOURCE: U.S. EPA and FDA data.

METHOD 3620A
FLORISIL COLUMN CLEANUP




A
B
Organochlorine pesticides, haloethers and organophosphorous
Nitroaromatics and isophorone
Type of analyte?
Chlorinated hydrocarbons
7 3 1 Reduce volume of sample extract to 2 mL
7 4 1 Reduce volume of sample extract to 2 mL
7 2 6 Add methanol to fraction; concentrate
7 3 2 Add Florisil to chromatographic column; add anhydrous sodium sulfate then hexane; discard eluate
7 5 1 Reduce volume of sample extract to 2 mL
7 4 2 Put Florisil slurry in chromatographic column, add anhydrous sodium sulfate
7 3 3 Adjust sample extract volume, transfer to column rinse with hexane
7 5 2 Place Florisil in chromatographic colum, add anhydrous sodium sulfate
7 4 3 Transfer sample extract onto column; add methylene chloride/hexane, discard eluate
7 3 4 Drain column, elute column 4 times into separate flasks
7 5 3 Preelute column with petroleum ether, transfer sample extract to column, discard eluate
7 4 4 Elute column with acetone/methylene chloride exchange solvent to hexane
7 3 5 Concentrate eluates; adjust volume
7 5 4 Concentrate fraction, adjust final volume
7 4 4 Concentrate fraction, adjust final volume
C
Analyze by GC

3630A

METHOD 3630A

SILICA GEL CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Silica gel is a regenerative adsorbent of amorphous silica with weakly acidic properties. It is produced from sodium silicate and sulfuric acid. Silica gel can be used for column chromatography and is for separating the analytes from interfering compounds of a different chemical polarity.

1.2 General applications (Gordon and Ford):

1.2.1 **Activated**: Heated at 150-160°C for several hours. USES: Separation of hydrocarbons.

1.2.2 **Deactivated**: Containing 10-20% water. USES: An adsorbent for most functionalities with ionic or nonionic characteristics, including alkaloids, sugar esters, glycosides, dyes, alkali metal cations, lipids, glycerides, steroids, terpenoids and plasticizers. The disadvantages of deactivated silica gel are that the solvents methanol and ethanol decrease adsorbent activity.

1.3 Specific applications: This method includes guidance for cleanup of sample extracts containing polynuclear aromatic hydrocarbons, derivatized phenolic compounds.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required amount of adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution of the analytes is effected with a suitable solvent(s) leaving the interfering compounds on the column. The eluate is then concentrated (if necessary).

3.0 INTERFERENCES

3.1 A reagent blank should be analyzed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Chromatographic column - 250 mm long x 10 mm ID; with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without

frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Beakers - 500 mL.

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.4 Vials - 10, 25 mL, glass with Teflon lined screw-caps or crimp tops.

4.5 Muffle furnace.

4.6 Reagent bottle - 500 mL.

4.7 Water bath - Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.8 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.9 Erlenmeyer flasks - 50 and 250 mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Silica gel. 100/200 mesh desiccant (Davison Chemical grade 923 or equivalent). Before use, activate for at least 16 hr. at 130°C in a shallow

glass tray, loosely covered with foil.

5.4 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.5 Eluting solvents

5.5.1 Cyclohexane, C_6H_{12} - Pesticide quality or equivalent.

5.5.2 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.5.3 2-Propanol, $(CH_3)_2CHOH$ - Pesticide quality or equivalent.

5.5.4 Toluene, $C_6H_5CH_3$ - Pesticide quality or equivalent.

5.5.5 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.5.6 Pentane, C_5H_{12} - Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Polynuclear aromatic hydrocarbons

7.1.1 Before the silica gel cleanup technique can be utilized, the extract solvent must be exchanged to cyclohexane. The exchange is performed as follows:

7.1.1.1 Following K-D concentration of the extract to 1-2 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 minutes. Add one or two clean boiling chips to the K-D flask. Add 4 mL of exchange solvent and attach a two ball micro-Snyder column. Prewet the Snyder column by adding about 0.5 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5-1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.1.1.2 Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of exchange solvent. Adjust the extract volume to about 2 mL.

7.1.2 Prepare a slurry of 10 g of activated silica gel in methylene chloride and place this into a 10 mm ID chromatographic column. Tap the column to settle the silica gel and elute the methylene chloride. Add 1 to 2 cm of anhydrous sodium sulfate to the top of the silica gel.

7.1.3 Preelute the column with 40 mL of pentane. The rate for all elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 2 mL cyclohexane sample extract onto the column using an additional 2 mL cyclohexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane and continue the elution of the column. Discard this pentane eluate.

7.1.4 Next, elute the column with 25 mL of methylene chloride/pentane (2:3)(v/v) into a 500 mL K-D flask equipped with a 10 mL concentrator tube. Concentrate the collected fraction to whatever volume is required (1-10 mL). Proceed with HPLC or GC analysis. Components that elute in this fraction are:

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(g,h,i)perylene
Benzo(k)fluoranthene
Chrysene
Dibenzo(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

7.2 Derivatized phenols

7.2.1 This silica gel cleanup procedure is performed on sample extracts that have undergone pentafluorobenzyl bromide derivatization as described in Method 8040.

7.2.2 Place 4.0 g of activated silica gel into a 10 mm ID chromatographic column. Tap the column to settle the silica gel and add about 2 g of anhydrous sodium sulfate to the top of the silica gel.

7.2.3 Preelute the column with 6 mL of hexane. The rate for all

elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, pipet onto the column 2 mL of the hexane solution that contains the derivatized sample or standard. Elute the column with 10.0 mL of hexane and discard the eluate.

7.2.4 Elute the column, in order, with 10.0 mL of 15% toluene in hexane (Fraction 1); 10.0 mL of 40% toluene in hexane (Fraction 2); 10.0 mL of 75% toluene in hexane (Fraction 3); and 10.0 mL of 15% 2-propanol in toluene (Fraction 4). All elution mixtures are prepared on a volume:volume basis. Elution patterns for the phenolic derivatives are shown in Table 1. Fractions may be combined, as desired, depending upon the specific phenols of interest or level of interferences. Proceed with GC analysis (Method 8040).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Table 1 provides performance information on the fractionation of phenolic derivatives using this method.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

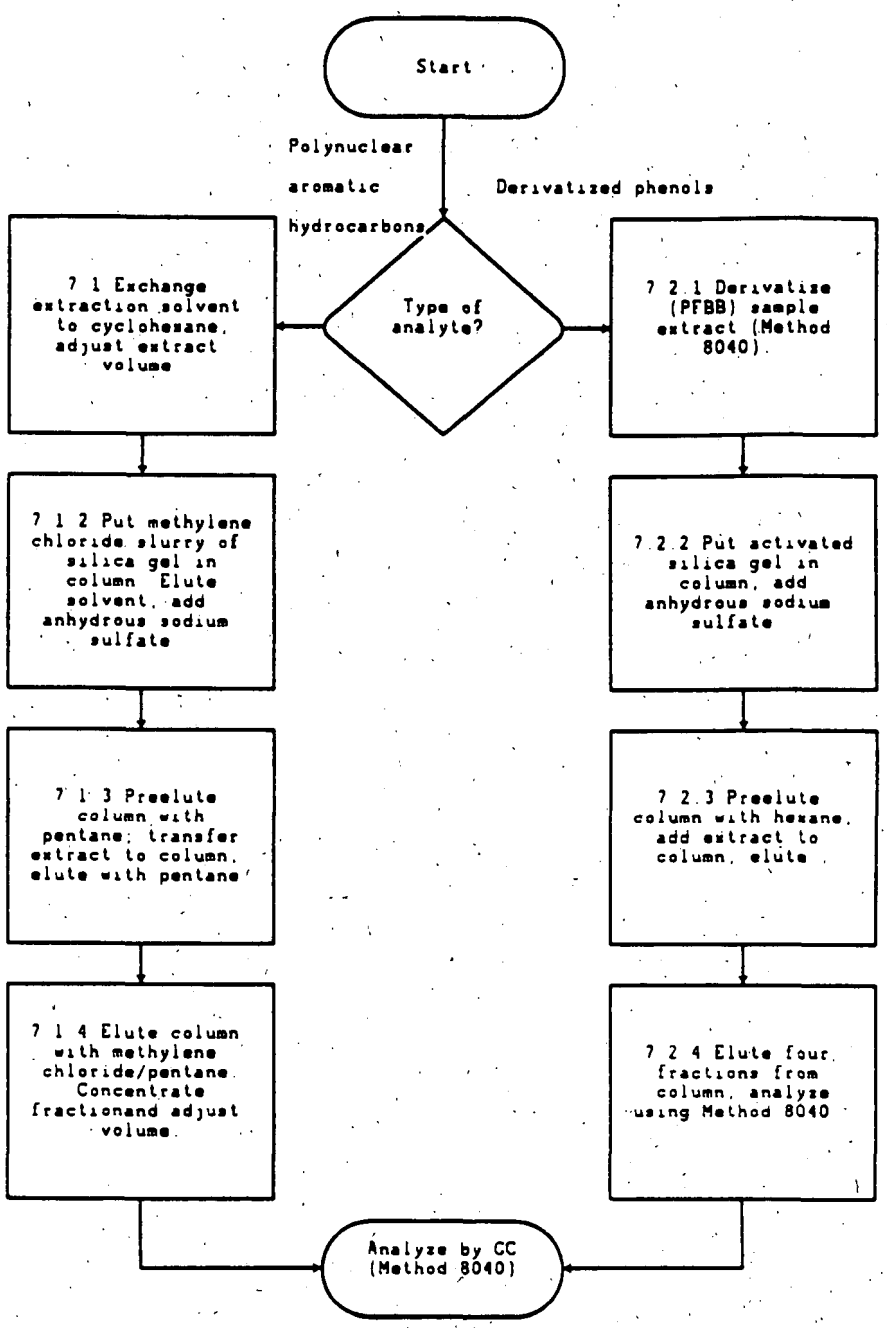
TABLE 1
SILICA GEL FRACTIONATION OF PFBB DERIVATIVES

Parameter	Percent Recovery by Fraction[a]			
	1	2	3	4
2-Chlorophenol		90	1	
2-Nitrophenol			9	90
Phenol		90	10	
2,4-Dimethylphenol		95	7	
2,4-Dichlorophenol		95	1	
2,4,6-Trichlorophenol	50	50		
4-Chloro-3-methylphenol		84	14	
Pentachlorophenol	75	20		
4-Nitrophenol			1	90

[a] Eluant composition:

Fraction 1 - 15% toluene in hexane.
Fraction 2 - 40% toluene in hexane.
Fraction 3 - 75% toluene in hexane.
Fraction 4 - 15% 2-propanol in toluene.

METHOD 3630A
SILICA GEL CLEANUP



3630B

METHOD 3630B

SILICA GEL CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Silica gel is a regenerative adsorbent of amorphous silica with weakly acidic properties. It is produced from sodium silicate and sulfuric acid. Silica gel can be used in column chromatography for the separation of analytes from interfering compounds of a different chemical polarity. It may be used activated, after heating to 150 - 160°C, or deactivated with up to 10% water.

1.2 This method includes guidance for standard column cleanup of sample extracts containing polynuclear aromatic hydrocarbons, derivatized phenolic compounds, organochlorine pesticides, and PCBs as Aroclors.

1.3 This method also provides cleanup procedures using solid-phase extraction cartridges for pentafluorobenzyl bromide-derivatized phenols, organochlorine pesticides, and PCBs as Aroclors. This technique also provides the best separation of PCBs from most single component organochlorine pesticides. When only PCBs are to be measured, this method can be used in conjunction with sulfuric acid/permanganate cleanup (Method 3665).

1.4 Other analytes may be cleaned up using this method if the analyte recovery meets the criteria specified in Sec. 8.0.

2.0 SUMMARY OF METHOD

2.1 This method provides the option of using either standard column chromatography techniques or solid-phase extraction cartridges. Generally, the standard column chromatography techniques use larger amounts of adsorbent and, therefore, have a greater cleanup capacity.

2.2 In the standard column cleanup protocol, the column is packed with the required amount of adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution of the analytes is accomplished with a suitable solvent(s) that leaves the interfering compounds on the column. The eluate is then concentrated (if necessary).

2.3 The cartridge cleanup protocol uses silica solid-phase extraction cartridges packed with 1 g or 2 g of adsorbent. Each cartridge is solvent washed immediately prior to use. Aliquots of sample extracts are loaded onto the cartridges, which are then eluted with suitable solvent(s). A vacuum manifold is required to obtain reproducible results. The collected fractions may be further concentrated prior to gas chromatographic analysis.

2.4 The appropriate gas chromatographic method is listed at the end of each technique. Analysis may also be performed by gas chromatography/mass spectrometry (Method 8270).

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks. See Sec. 8 for guidance on a reagent blank check.

3.2 Phthalate ester contamination may be a problem with certain cartridges The more inert the column and/or cartridge material (i.e., glass or Teflon), the less problem with phthalates. Phthalates create interference problems for all method analytes, not just the phthalate esters themselves.

3.3 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Chromatographic column - 250 mm long x 10 mm ID; with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Beakers - 500 mL.

4.3 Vials - 2, 10, 25 mL, glass with Teflon lined screw-caps or crimp tops.

4.4 Muffle furnace.

4.5 Reagent bottle - 500 mL.

4.6 Erlenmeyer flasks - 50 and 250 mL.

4.7 Vacuum manifold: VacElute Manifold SPS-24 (Analytichem International), Visiprep (Supelco, Inc.) or equivalent, consisting of glass vacuum basin, collection rack and funnel, collection vials, replaceable stainless steel delivery tips, built-in vacuum bleed valve and gauge. The system is connected to a vacuum pump or water aspirator through a vacuum trap made from a 500 mL sidearm flask fitted with a one-hole stopper and glass tubing.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used,

provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Silica gel for chromatography columns.

5.3.1 Silica Gel for Phenols and Polynuclear Aromatic Hydrocarbons: 100/200 mesh desiccant (Davison Chemical grade 923 or equivalent). Before use, activate for at least 16 hr. at 130°C in a shallow glass tray, loosely covered with foil.

5.3.2 Silica Gel for Organochlorine pesticides/PCBs: 100/200 mesh desiccant (Davison Chemical grade 923 or equivalent). Before use, activate for at least 16 hr. at 130°C in a shallow glass tray, loosely covered with foil. Deactivate it to 3.3% with reagent water in a 500 mL glass jar. Mix the contents thoroughly and allow to equilibrate for 6 hours. Store the deactivated silica gel in a sealed glass jar inside a desiccator.

5.4 Silica cartridges: 40 μm particles, 60 A pores. The cartridges with which this method was developed consist of 6 mL serological-grade polypropylene tubes, with the 1 g of silica held between two polyethylene or stainless steel frits with 20 μm pores. 2 g silica cartridges are also used in this method, and 0.5 g cartridges are available. The compound elution patterns must be verified when cartridges other than the specified size are used.

5.5 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. A method blank must be analyzed in order to demonstrate that there is no interference from the sodium sulfate.

5.6 Eluting solvents

5.6.1 Cyclohexane, C_6H_{12} - Pesticide quality or equivalent.

5.6.2 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.6.3 2-Propanol, $(CH_3)_2CHOH$ - Pesticide quality or equivalent.

5.6.4 Toluene, $C_6H_5CH_3$ - Pesticide quality or equivalent.

5.6.5 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.6.6 Pentane, C_5H_{12} - Pesticide quality or equivalent.

5.6.7 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.6.8 Diethyl Ether, $C_2H_5OC_2H_5$. Pesticide quality or equivalent. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the

test strips. After cleanup, 20 mL of ethanol preservative must be added to each liter of ether.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 General Guidance

7.1.1 The procedure contains two cleanup options for the derivatized phenols and organochlorine pesticides/Aroclors, but only one technique for the polynuclear aromatic hydrocarbons (PAHs) (standard column chromatography). Cleanup techniques by standard column chromatography for all analytes are found in Sec. 7.2. Cleanup techniques by solid-phase cartridges for derivatized phenols and PAHs are found in Sec. 7.3. The standard column chromatography techniques are packed with a greater amount of silica gel adsorbent and, therefore, have a greater cleanup capacity. A rule of thumb relating to cleanup capacity is that 1 g of sorbent material will remove 10 to 30 mg of total interferences. (However, capacity is also dependent on the sorbent retentiveness of the interferences.) Therefore, samples that exhibit a greater degree of sample interference should be cleaned up by the standard column technique. However, both techniques have limits on the amount of interference that can be removed. If the interference is caused by high boiling material, then Method 3640 should be used prior to this method. If the interference is caused by relatively polar compounds of the same boiling range as the analytes, then multiple column or cartridge cleanups may be required. If crystals of sulfur are noted in the extract, then Method 3660 should be utilized prior to this method. The cartridge cleanup techniques are often faster and use less solvent, however they have less cleanup capacity.

7.1.2 Allow the extract to reach room temperature if it was in cold storage. Inspect the extracts visually to ensure that there are no particulates or phase separations and that the volume is as stated in the accompanying documents. Verify that the solvent is compatible with the cleanup procedures. If crystals of sulfur are visible or if the presence of sulfur is suspected, proceed with Method 3660.

7.1.3 If the extract solvent is methylene chloride, for most cleanup techniques, it must be exchanged to hexane. (For the PAHs, exchange to cyclohexane as per Sec. 7.2.1). Follow the standard Kuderna-Danish concentration technique provided in each extraction method. The volume of methylene chloride should have been reduced to 1 - 2 mL. Add 40 mL of hexane, a fresh boiling chip and repeat the concentration as written. The final volume required for the cleanup techniques is normally 2 mL.

7.2 Standard Column Cleanup Techniques

7.2.1 Polynuclear aromatic hydrocarbons

7.2.1.1 Before the silica gel cleanup technique can be utilized, the extract solvent must be exchanged to cyclohexane. The exchange is performed by adding 4 mL of cyclohexane following reduction of the sample extract to 1-2 mL using the macro Snyder column. Attach the two ball micro Snyder column and reduce the volume to 2 mL.

> CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost. If the extract goes to dryness, the extraction must be repeated.

7.2.1.2 Prepare a slurry of 10 g of activated silica gel (Sec. 5.3.1) in methylene chloride and place this into a 10 mm ID chromatographic column. Tap the column to settle the silica gel and elute the methylene chloride. Add 1 to 2 cm of anhydrous sodium sulfate to the top of the silica gel.

7.2.1.3 Pre-elute the column with 40 mL of pentane. The rate for all elutions should be about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, transfer the 2 mL cyclohexane sample extract onto the column using an additional 2 mL cyclohexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane and continue the elution of the column. Discard this pentane eluate.

7.2.1.4 Next, elute the column with 25 mL of methylene chloride/pentane (2:3)(v/v) into a 500 mL K-D flask equipped with a 10 mL concentrator tube. Concentrate the collected fraction to whatever volume is required (1-10 mL). Proceed with HPLC (Method 8310) or GC analysis (Method 8100). Validated components that elute in this fraction are:

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(g,h,i)perylene
Benzo(k)fluoranthene
Chrysene
Dibenzo(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

7.2.2 Derivatized Phenols

7.2.2.1 This silica gel cleanup procedure is performed on sample extracts that have undergone pentafluorobenzyl bromide derivatization, as described in Method 8040. The sample extract must be in 2 mL of hexane at this point.

7.2.2.2 Place 4.0 g of activated silica gel (Sec. 5.3.1) into a 10 mm ID chromatographic column. Tap the column to settle the silica gel and add about 2 g of anhydrous sodium sulfate to the top of the silica gel.

7.2.2.3 Pre-elute the column with 6 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, pipet onto the column 2 mL of the hexane solution that contains the derivatized sample or standard. Elute the column with 10.0 mL of hexane and discard the eluate.

7.2.2.4 Elute the column, in order, with 10.0 mL of 15% toluene in hexane (Fraction 1); 10.0 mL of 40% toluene in hexane (Fraction 2); 10.0 mL of 75% toluene in hexane (Fraction 3); and 10.0 mL of 15% 2-propanol in toluene (Fraction 4). All elution mixtures are prepared on a volume:volume basis. Elution patterns for the phenolic derivatives are shown in Table 1. Fractions may be combined, as desired, depending upon the specific phenols of interest or level of interferences. Proceed with GC analysis (Method 8040).

7.2.3 Organochlorine Pesticides and Aroclors

7.2.3.1 Transfer a 3 g portion of deactivated silica gel (Sec. 5.3.2) into a 10 mm ID glass chromatographic column and top it with 2 to 3 cm of anhydrous sodium sulfate.

7.2.3.2 Add 10 mL of hexane to the top of the column to wet and rinse the sodium sulfate and silica gel. Just prior to exposure of the sodium sulfate layer to air, stop the hexane eluate flow by closing the stopcock on the chromatographic column. Discard the eluate.

7.2.3.3 Transfer the sample extract (2 mL in hexane) onto the column. Rinse the extract vial twice with 1 to 2 mL of hexane and add each rinse to the column. Elute the column with 80 mL of hexane (Fraction I) at a rate of about 5 mL/min. Remove the collection flask and set it aside for later concentration. Elute the column with 50 mL of hexane (Fraction II) and collect the eluate. Perform a third elution with 15 mL of methylene chloride (Fraction III). The elution patterns for the organochlorine pesticides, Aroclor-1016, and Aroclor-1260 are shown in Table 2.

7.2.3.4 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. Fractions may be combined, as desired, depending upon the specific

pesticides/Aroclors of interest or level of interferences. If mixtures of Aroclors and pesticides are expected, it is best to analyze Fraction I separately, since it contains the Aroclors separated from most pesticides. Proceed with GC analysis as per Method 8081.

7.3 Cartridge Cleanup Techniques

7.3.1 Cartridge Set-up and Conditioning

7.3.1.1 Arrange the 1 g silica cartridges (2 g for phenol cleanup) on the manifold in the closed-valve position. Other size cartridges may be used, however the data presented in the Tables are all based on 1 g cartridges for pesticides/Aroclors and 2 g cartridges for phenols. Therefore, supporting recovery data must be developed for other sizes. Larger cartridges will probably require larger volumes of elution solvents.

7.3.1.2 Turn on the vacuum pump and set pump vacuum to 10 inches (254 mm) of Hg. Do not exceed the manufacturer's recommendation for manifold vacuum. Flow rates can be controlled by opening and closing cartridge valves.

7.3.1.3 Condition the cartridges by adding 4 mL of hexane to each cartridge. Slowly open the cartridge valves to allow hexane to pass through the sorbent beds to the lower frits. Allow a few drops per cartridge to pass through the manifold to remove all air bubbles. Close the valves and allow the solvent to soak the entire sorbent bed for 5 minutes. Do not turn off the vacuum.

7.3.1.4 Slowly open cartridge valves to allow the hexane to pass through the cartridges. Close the cartridge valves when there is still at least 1 mm of solvent above the sorbent bed. Do not allow cartridges to become dry. If cartridges go dry, repeat the conditioning step.

7.3.2 Derivatized Phenols

7.3.2.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane and the phenols must have undergone derivatization by pentafluorobenzyl bromide, as per Method 8040.

7.3.2.2 Transfer the extract to the 2 g cartridge that has been conditioned as described in Sec. 7.3.1. Open the cartridge valve to allow the extract to pass through the cartridge bed at approximately 2 mL/minute.

7.3.2.3 When the entire extract has passed through the cartridges, but before the cartridge becomes dry, rinse the sample vials with an additional 0.5 mL of hexane, and add the rinse to the cartridges to complete the quantitative transfer.

7.3.2.4 Close the cartridge valve and turn off the vacuum after the solvent has passed through, ensuring that the cartridge never gets dry.

7.3.2.5 Place a 5 mL vial or volumetric flask into the sample rack corresponding to the cartridge position. Attach a solvent-rinsed stainless steel solvent guide to the manifold cover and align with the collection vial.

7.3.2.6 Add 5 mL of hexane to the cartridge. Turn on the vacuum pump and adjust the pump pressure to 10 inches (254 mm) of Hg. Allow the solvent to soak the sorbent bed for 1 minute or less. Slowly open the cartridge valve, and collect the eluate (this is Fraction 1, and should be discarded).

NOTE: If cartridges smaller than 2 g are used, then Fraction 1 cannot be discarded, since it contains some of the phenols.

7.3.2.7 Close the cartridge valve, replace the collection vial, and add 5 mL of toluene/hexane (25/75, v/v) to the cartridge. Slowly open the cartridge valve and collect the eluate into the collection vial. This is Fraction 2, and should be retained for analysis.

7.3.2.8 Adjust the final volume of the eluant to a known volume which will result in analyte concentrations appropriate for the project requirements (normally 1 - 10 mL). Table 3 shows compound recoveries for 2 g silica cartridges. The cleaned up extracts are ready for analysis by Method 8040.

7.3.3 Organochlorine Pesticides/Aroclors

NOTE: The silica cartridge procedure is appropriate when polychlorinated biphenyls are known to be present.

7.3.3.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.3.3.2 Use the 1 g cartridges conditioned as described in Sec. 7.3.1.

7.3.3.3 Transfer the extract to the cartridge. Open the cartridge valve to allow the extract to pass through the cartridge bed at approximately 2 mL/minute.

7.3.3.4 When the entire extract has passed through the cartridges, but before the cartridge becomes dry, rinse the sample vials with an additional 0.5 mL of solvent, and add the rinse to the cartridges to complete the quantitative transfer.

7.3.3.5 Close the cartridge valve and turn off the vacuum after the solvent has passed through, ensuring that the cartridge never goes dry.

7.3.3.6 Place a 5 mL vial or volumetric flask into the sample rack corresponding to the cartridge position. Attach a solvent-rinsed stainless steel solvent guide to the manifold cover and align with the collection vial.

7.3.3.7 Add 5 mL of hexane to the cartridge. Turn on the vacuum pump and adjust the pump pressure to 10 inches (254 mm) of Hg. Allow the solvent to soak the sorbent bed for 1 minute or less. Slowly open the cartridge valve and collect the eluate into the collection vial (Fraction 1).

7.3.3.8 Close the cartridge valve, replace the collection vial, and add 5 mL of diethyl ether/hexane (50/50, v/v) to the cartridge. Slowly open the cartridge valve and collect the eluate into the collection vial (Fraction 2).

7.3.3.9 Adjust the final volume of each of the two fractions to a known volume which will result in analyte concentrations appropriate for the project requirements (normally 1 - 10 mL). The fractions may be combined prior to final adjustment of volume, if analyte fractionation is not required. Table 4 shows compound recoveries for 1 g silica cartridges. The cleaned up extracts are ready for analysis by Method 8081.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 A reagent blank (consisting of the elution solvents) must be passed through the column or cartridge and checked for the compounds of interest, prior to the use of this method. This same performance check is required with each new lot of adsorbent or cartridges. The level of interferences must be below the method detection limit before this method is performed on actual samples.

8.3 The analyst must demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples. See the attached Tables for acceptable recovery data. For compounds that have not been tested, recovery must be $\geq$ 85%.

8.3.1 Before any samples are processed using the solid-phase extraction cartridges, the efficiency of the cartridge must be verified. A recovery check must be performed using standards of the target analytes at known concentration. Only lots of cartridges that meet the recovery criteria for the spiked compounds can be used to process the samples.

8.3.2 A check should also be performed on each individual lot of cartridges and for every 300 cartridges of a particular lot.

8.4 For sample extracts that are cleaned up using this method, the associated quality control samples should also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Table 1 provides performance information on the fractionation of phenolic derivatives using standard column chromatography.

9.2 Table 2 provides performance information on the fractionation of organochlorine pesticides/Aroclors using standard column chromatography.

9.3 Table 3 shows recoveries of derivatized phenols obtained using 2 g silica cartridges.

9.4 Table 4 shows recoveries and fractionation of organochlorine pesticides obtained using 1 g silica cartridges.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

2. U.S EPA "Evaluation of Sample Extract Cleanup Using Solid-Phase Extraction Cartridges," Project Report, December 1989.

TABLE 1
SILICA GEL FRACTIONATION OF PFBB DERIVATIVES

Parameter	Percent Recovery by Fraction[a]			
	1	2	3	4
2-Chlorophenol		90	1	
2-Nitrophenol			9	90
Phenol		90	10	
2,4-Dimethylphenol		95	7	
2,4-Dichlorophenol		95	1	
2,4,6-Trichlorophenol	50	50		
4-Chloro-3-methylphenol		84	14	
Pentachlorophenol	75	20		
4-Nitrophenol			1	90

[a] Eluant composition:

Fraction 1 - 15% toluene in hexane.
Fraction 2 - 40% toluene in hexane.
Fraction 3 - 75% toluene in hexane.
Fraction 4 - 15% 2-propanol in toluene.

Data from Reference 1 (Method 604)

TABLE 2
DISTRIBUTION AND PERCENT RECOVERIES OF ORGANOCHLORINE PESTICIDES AND PCBs AS AROCLORS IN SILICA GEL COLUMN FRACTIONS[a,b,c,d,e]

Compound	Fraction I		Fraction II		Fraction III		Total Recovery	
	Conc. 1	Conc. 2	Conc. 1	Conc. 2	Conc. 1	Conc. 2	Conc. 1	Conc. 2
alpha-BHC[f]					82(1.7)	74(8.0)	82(1.7)	74(8.0)
beta-BHC					107(2.1)	98(12.5)	107(2.1)	98(12.5)
gamma-BHC					91(3.6)	85(10.7)	91(3.6)	85(10.7)
delta-BHC					92(3.5)	83(10.6)	92(3.5)	83(10.6)
Heptachlor	109(4.1)	118(8.7)					109(4.1)	118(8.7)
Aldrin	97(5.6)	104(1.6)					97(5.6)	104(1.6)
Heptachlor epoxide					95(4.7)	88(10.2)	95(4.7)	88(10.2)
Technical chlordane	14(5.5)	22(5.3)	19(6.8)	39(3.6)	29(5.0)	37(5.1)	62(3.3)	98(1.9)
Endosulfan I					95(5.1)	87(10.2)	95(5.1)	87(10.2)
4,4′-DDE	86(5.4)	94(2.8)					86(5.4)	94(2.8)
Dieldrin					96(6.0)	87(10.6)	96(6.0)	87(10.6)
Endrin					85(10.5)	71(12.3)	85(10.5)	71(12.3)
Endosulfan II					97(4.4)	86(10.4)	97(4.4)	86(10.4)
4,4′-DDD[f]					102(4.6)	92(10.2)	102(4.6)	92(10.2)
Endrin aldehyde					81(1.9)	76(9.5)	81(1.9)	76(9.5)
Endosulfan sulfate					93(4.9)	82(9.2)	93(4.9)	82(9.2)
4,4′-DDT[f]			86(13.4)	73(9.1)	15(17.7)	8.7(15.0)	101(5.3)	82(23.7)
4,4′-Methoxychlor					99(9.9)	82(10.7)	99(9.9)	82(10.7)
Toxaphene[f]			15(2.4)	17(1.4)	73(9.4)	84(10.7)	88(12.0)	101(10.1)
Aroclor-1016	86(4.0)	87(6.1)					86(4.0)	87(6.1)
Aroclor-1260	91(4.1)	95(5.0)					91(4.1)	95(5.0)

TABLE 2
(Continued)

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[a] Effluent composition: Fraction I, 80 mL hexane; Fraction II, 50 mL hexane; Fraction III, 15 mL methylene chloride.

[b] Concentration 1 is 0.5 µg per column for BHCs, Heptachlor, Aldrin, Heptachlor epoxide, and Endosulfan I; 1.0 µg per column for Dieldrin, Endosulfan II, 4,4′-DDD, 4,4′-DDE, 4,4′-DDT, Endrin, Endrin aldehyde, and Endosulfan sulfate; 5 µg per column for 4,4′-Methoxychlor and technical Chlordane; 10 µg per column for Toxaphene, Aroclor-1016, and Aroclor-1260.

[c] For Concentration 2, the amounts spiked are 10 times as high as those for Concentration 1.

[d] Values given represent the average recovery of three determinations; numbers in parentheses are the standard deviation; recovery cutoff point is 5 percent.

[e] Data obtained with standards, as indicated in footnotes b and c, dissolved in 2 mL hexane.

[f] It has been found that because of batch-to-batch variation in the silica gel material, these compounds cross over in two fractions and the amounts recovered in each fraction are difficult to reproduce.

TABLE 3
PERCENT RECOVERIES AND ELUTION PATTERNS FOR 18 PHENOLS FROM 2 g SILICA CARTRIDGES[a]

Compound	Fraction 2 Average Recovery	Fraction 2 Percent RSD
Phenol	74.1	5.2
2-Methylphenol	84.8	5.2
3-Methylphenol	86.4	4.4
4-Methylphenol	82.7	5.0
2,4-Dimethylphenol	91.8	5.6
2-Chlorophenol	88.5	5.0
2,6-Dichlorophenol	90.4	4.4
4-Chloro-3-methylphenol	94.4	7.1
2,4-Dichlorophenol	94.5	7.0
2,4,6-Trichlorophenol	97.8	6.6
2,3,6-Trichlorophenol	95.6	7.1
2,4,5-Trichlorophenol	92.3	8.2
2,3,5-Trichlorophenol	92.3	8.2
2,3,5,6-Tetrachlorophenol	97.5	5.3
2,3,4,6-Tetrachlorophenol	97.0	6.1
2,3,4-Trichlorophenol	72.3	8.7
2,3,4,5-Tetrachlorophenol	95.1	6.8
Pentachlorophenol	96.2	8.8

[a] Silica cartridges (Supelco, Inc.) were used; each cartridge was conditioned with 4 mL of hexane prior to use. Each experiment was performed in duplicate at three spiking concentrations (0.05 µg, 0.2 µg, and 0.4 µg per compound per cartridge). Fraction 1 was eluted with 5 mL hexane and was discarded. Fraction 2 was eluted with 5 mL toluene/hexane (25/75, v/v).

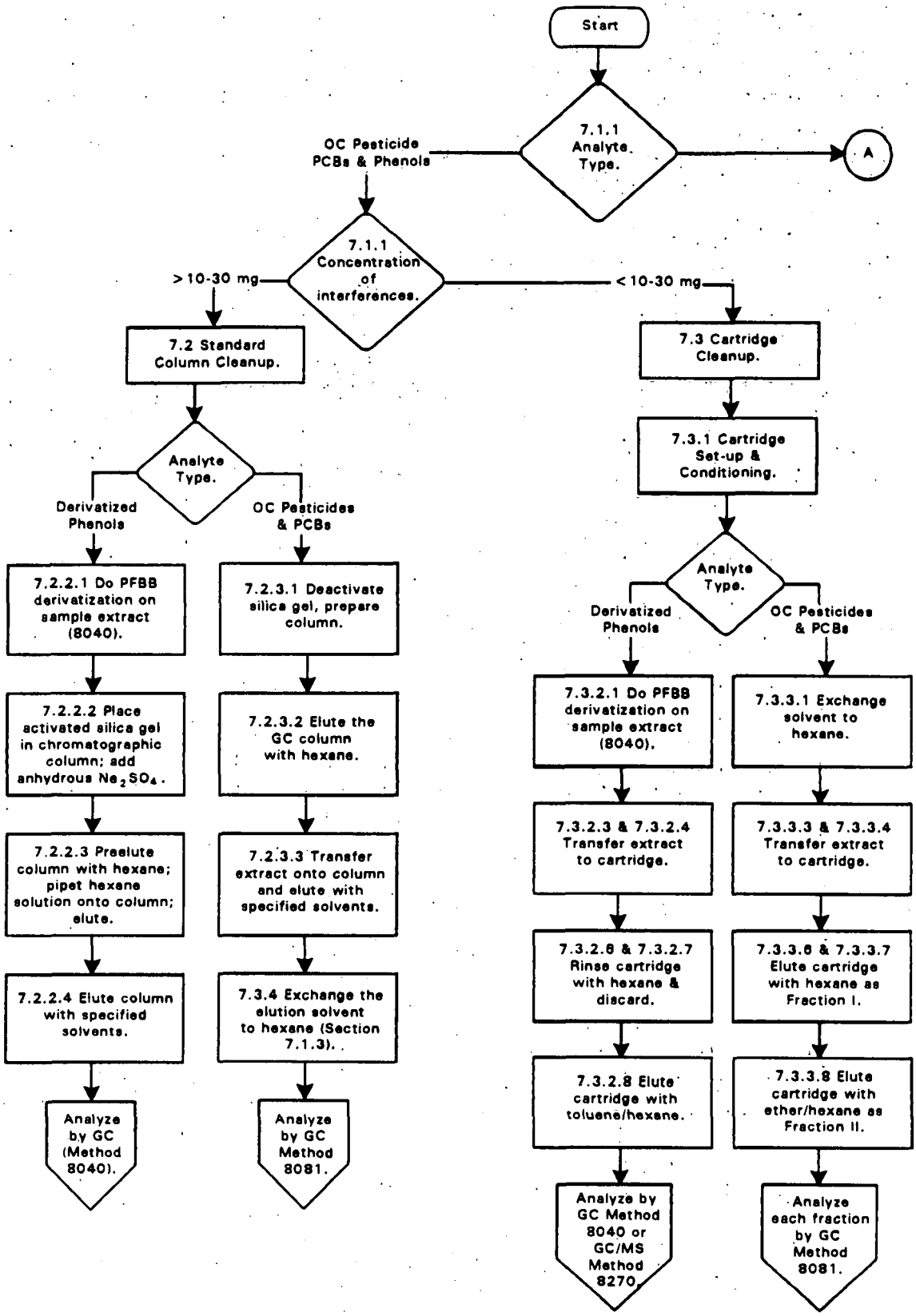
Data from Reference 2

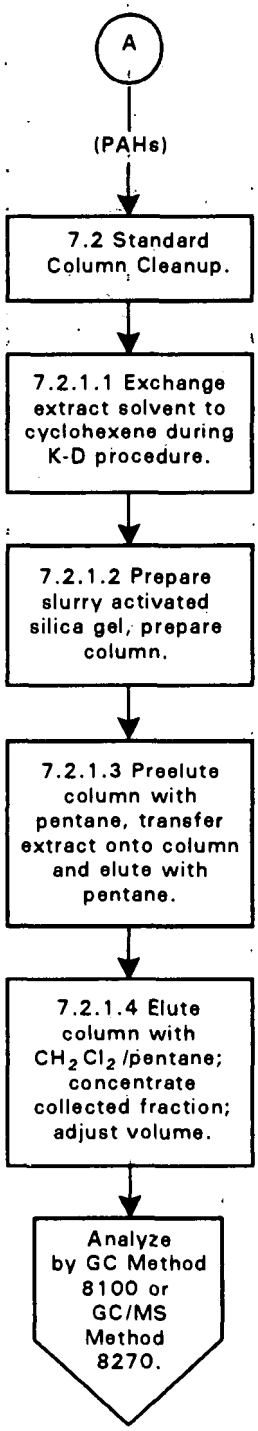
TABLE 4
PERCENT RECOVERIES AND ELUTION PATTERNS FOR 17 ORGANOCHLORINE PESTICIDES AND AROCLORS FROM 1 g SILICA CARTRIDGES[a]

Compound	Fraction 1 Average Recovery	Fraction 1 Percent RSD	Fraction 2 Average Recovery	Fraction 2 Percent RSD
alpha-BHC	0		98.7	2.3
gamma-BHC	0		94.8	1.9
beta-BHC	0		94.3	3.0
Heptachlor	97.3	1.3	0	
delta-BHC	0		90.8	2.5
Aldrin	95.9	1.0	0	
Heptachlor epoxide	0		97.9	2.1
Endosulfan I	0		102	2.3
4,4′-DDE	99.9	1.7	0	
Dieldrin	0		92.3	2.0
Endrin	0		117	2.6
4,4′-DDD	10.7	41	92.4	3.3
Endosulfan II	0		96.0	2.2
4,4′-DDT	94.1	2.0	0	
Endrin aldehyde	0		59.7	2.6
Endosulfan sulfate	0		97.8	2.1
4,4′-Methoxychlor	0		98.0	2.4
Aroclor 1016	124			
Aroclor 1221	93.5			
Aroclor 1232	118			
Aroclor 1242	116			
Aroclor 1248	114			
Aroclor 1254	108			
Aroclor 1264	112			

[a] Silica cartridges (Supelco, Inc. lot SP0161) were used; each cartridge was conditioned with 4 mL hexane prior to use. The organochlorine pesticides were tested separately from PCBs. Each organochlorine pesticides experiment was performed in duplicate, at three spiking concentrations (0.2 µg, 1.0 µg, and 2.0 µg per compound per cartridge). Fraction 1 was eluted with 5 mL of hexane, Fraction 2 with 5 mL of diethyl ether/hexane (50/50, v/v). PCBs were spiked at 10 µg per cartridge and were eluted with 3 mL of hexane. The values given for PCBs are the percent recoveries for a single determination.

Data from Reference 2


Start
7.1.1 Analyte Type.
OC Pesticide PCBs & Phenols
A
7.1.1 Concentration of interferences.
> 10-30 mg
< 10-30 mg
7.2 Standard Column Cleanup.
Analyte Type.
Derivatized Phenols
OC Pesticides & PCBs
7.2.2.1 Do PFBB derivatization on sample extract (8040).
7.2.2.2 Place activated silica gel in chromatographic column; add anhydrous Na_2SO_4.
7.2.2.3 Preelute column with hexane; pipet hexane solution onto column; elute.
7.2.2.4 Elute column with specified solvents.
Analyze by GC (Method 8040).
7.2.3.1 Deactivate silica gel, prepare column.
7.2.3.2 Elute the GC column with hexane.
7.2.3.3 Transfer extract onto column and elute with specified solvents.
7.3.4 Exchange the elution solvent to hexane (Section 7.1.3).
Analyze by GC Method 8081.
7.3 Cartridge Cleanup.
7.3.1 Cartridge Set-up & Conditioning.
Analyte Type.
Derivatized Phenols
OC Pesticides & PCBs
7.3.2.1 Do PFBB derivatization on sample extract (8040).
7.3.2.3 & 7.3.2.4 Transfer extract to cartridge.
7.3.2.6 & 7.3.2.7 Rinse cartridge with hexane & discard.
7.3.2.8 Elute cartridge with toluene/hexane.
Analyze by GC Method 8040 or GC/MS Method 8270.
7.3.3.1 Exchange solvent to hexane.
7.3.3.3 & 7.3.3.4 Transfer extract to cartridge.
7.3.3.6 & 7.3.3.7 Elute cartridge with hexane as Fraction I.
7.3.3.8 Elute cartridge with ether/hexane as Fraction II.
Analyze each fraction by GC Method 8081.


A
(PAHs)
7.2 Standard Column Cleanup.
7.2.1.1 Exchange extract solvent to cyclohexene during K-D procedure.
7.2.1.2 Prepare slurry activated silica gel, prepare column.
7.2.1.3 Preelute column with pentane, transfer extract onto column and elute with pentane.
7.2.1.4 Elute column with CH_2Cl_2/pentane; concentrate collected fraction; adjust volume.
Analyze by GC Method 8100 or GC/MS Method 8270.

METHOD 3640A

GEL-PERMEATION CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Gel-permeation chromatography (GPC) is a size exclusion cleanup procedure using organic solvents and hydrophobic gels in the separation of synthetic macromolecules (1). The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be larger than the molecular size of the molecules to be separated (2). A cross-linked divinylbenzene-styrene copolymer (SX-3 Bio Beads or equivalent) is specified for this method.

1.2 General cleanup application - GPC is recommended for the elimination from the sample of lipids, polymers, copolymers, proteins, natural resins and polymers, cellular components, viruses, steroids, and dispersed high-molecular-weight compounds (2). GPC is appropriate for both polar and non-polar analytes, therefore, it can be effectively used to cleanup extracts containing a broad range of analytes.

1.3 Specific application - This method includes guidance for cleanup of sample extracts containing the following analytes from the RCRA Appendix VIII and Appendix IX lists:

Compound Name	CAS No.[a]
Acenaphthene	83-32-9
Acenaphthylene	208-96-8
Acetophenone	98-86-2
2-Acetylaminofluorene	53-96-3
Aldrin	309-00-2
4-Aminobiphenyl	92-67-1
Aniline	62-53-3
Anthracene	120-12-7
Benomyl	17804-35-2
Benzenethiol	108-98-5
Benzidine	92-87-5
Benz(a)anthracene	56-55-3
Benzo(b)fluoranthene	205-99-2
Benzo(a)pyrene	50-32-8
Benzo(ghi)perylene	191-24-2
Benzo(k)fluoranthene	207-08-9
Benzoic acid	65-85-0
Benzotrichloride	98-07-7
Benzyl alcohol	100-51-6
Benzyl chloride	100-44-7
alpha-BHC	319-84-6
beta-BHC	319-85-7

Compound Name	CAS No.[a]
gamma-BHC	58-89-9
delta-BHC	319-86-8
4-Bromophenyl phenyl ether	101-55-3
Butyl benzyl phthalate	85-68-7
2-sec-butyl-4,6-dinitrophenol (Dinoseb)	88-85-7
Carbazole	86-74-8
Carbendazim	10605-21-7
alpha-Chlordane	5103-71-9
gamma-Chlordane	5566-34-7
4-Chloro-3-methylphenol	59-50-7
4-Chloroaniline	106-47-8
Chlorobenzilate	510-15-6
Bis(2-chloroethoxy)methane	111-91-1
Bis(2-chloroethyl) ether	111-44-4
Bis(2-chloroisopropyl) ether	108-60-1
2-Chloronaphthalene	91-58-7
2-Chlorophenol	95-57-8
4-Chlorophenol	106-48-9
3-Chlorophenol	108-43-0
4-Chlorophenyl phenyl ether	7005-72-3
3-Chloropropionitrile	542-76-7
Chrysene	218-01-9
2-Cresol	95-48-7
3-Cresol	108-39-4
4-Cresol	106-44-5
Cyclophosphamide	50-18-0
DDD	72-54-8
DDE	72-55-9
DDT	50-29-3
Di-n-butyl phthalate	84-74-2
Diallate	2303-16-4
Dibenzo(a,e)pyrene	192-65-4
Dibenzo(a,i)pyrene	189-55-9
Dibenz(a,j)acridine	224-42-0
Dibenz(a,h)anthracene	53-70-3
Dibenzofuran	132-64-9
Dibenzothiophene	132-65-0
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
trans-1,4-Dichloro-2-butene	110-57-6
cis-1,4-Dichloro-2-butene	1476-11-5
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	106-46-7
1,4-Dichlorobenzene	541-73-1
3,3'-Dichlorobenzidine	91-94-1
2,6-Dichlorophenol	87-65-0
2,4-Dichlorophenoxyacetic acid (2,4-D)	94-75-7
2,4-Dichlorophenol	120-83-2

Compound Name	CAS No.[a]
2,4-Dichlorotoluene	95-73-8
1,3-Dichloro-2-propanol	96-23-1
Dieldrin	60-57-1
Diethyl phthalate	84-66-2
Dimethoate	60-51-5
Dimethyl phthalate	131-11-3
p-Dimethylaminoazobenzene	60-11-7
7,12-Dimethyl-benz(a)anthracene	57-97-6
2,4-Dimethylphenol	105-67-9
3,3-Dimethylbenzidine	119-93-7
4,6-Dinitro-o-cresol	534-52-1
1,3-Dinitrobenzene	99-65-0
2,4-Dinitrophenol	51-28-5
2,4-Dinitrotoluene	121-14-2
2,6-Dinitrotoluene	606-20-2
Diphenylamine	122-39-4
Diphenyl ether	101-84-8
1,2-Diphenylhydrazine	122-66-7
Disulfoton	298-04-4
Endosulfan sulfate	1031-07-8
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Endrin ketone	53494-70-5
Ethyl methane sulfonate	62-50-0
Ethyl methacrylate	97-63-2
Bis(2-ethylhexyl) phthalate	117-81-7
Famphur	52-85-7
Fluorene	86-73-7
Fluoranthene	206-44-0
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Hexachlorobutadiene	87-68-3
Hexachlorocyclopentadiene	77-47-4
Hexachloroethane	67-72-1
Hexachloropropene	1888-71-7
Indeno(1,2,3-cd)pyrene	193-39-5
Isodrin	465-73-6
Isophorone	78-59-1
cis-Isosafrole	17627-76-8
trans-Isosafrole	4043-71-4
Kepone	143-50-0
Malononitrile	109-77-3
Merphos	150-50-5
Methoxychlor	72-43-5
3-Methylcholanthrene	56-49-5

Compound Name	CAS No.[a]
2-Methylnaphthalene	91-57-6
Methyl parathion	298-00-0
4,4′-Methylene-bis(2-chloroaniline)	101-14-4
Naphthalene	91-20-3
1,4-Naphthoquinone	130-15-4
2-Naphthylamine	91-59-8
1-Naphthylamine	134-32-7
5-Nitro-o-toluidine	99-55-8
2-Nitroaniline	88-74-4
3-Nitroaniline	99-09-2
4-Nitroaniline	100-01-6
Nitrobenzene	98-95-3
2-Nitrophenol	79-46-9
4-Nitrophenol	100-02-7
N-Nitrosodi-n-butylamine	924-16-3
N-Nitrosodiethanolamine	1116-54-7
N-Nitrosodiethylamine	55-18-5
N-Nitrosodimethylamine	62-75-9
N-Nitrosodiphenylamine	86-30-6
N-Nitrosodi-n-propylamine	621-64-7
N-Nitrosomethylethylamine	10595-95-6
N-Nitrosomorpholine	59-89-2
N-Nitrosopiperidine	100-75-4
N-Nitrosopyrolidine	930-55-2
Di-n-octyl phthalate	117-84-0
Parathion	56-38-2
Pentachlorobenzene	608-93-5
Pentachloroethane	76-01-7
Pentachloronitrobenzene (PCNB)	82-68-8
Pentachlorophenol	87-86-5
Phenacetin	62-44-2
Phenanthrene	85-01-8
Phenol	108-95-2
1,2-Phenylenediamine	95-54-5
Phorate	298-02-2
2-Picoline	109-06-8
Pronamide	23950-58-5
Pyrene	129-00-0
Resorcinol	108-46-3
Safrole	94-59-7
1,2,4,5-Tetrachlorobenzene	95-94-3
2,3,5,6-Tetrachloronitrobenzene	117-18-0
2,3,5,6-Tetrachlorophenol	935-95-5
2,3,4,6-Tetrachlorophenol	58-90-2
Tetraethyl dithiopyrophosphate (Sulfotep)	3689-24-5
Thiosemicarbazide	79-19-6
2-Toluidine	106-49-0
4-Toluidine	95-53-4

Compound Name	CAS No.[a]
Thiourea, 1-(o-chlorophenyl)	5344-82-1
Toluene-2,4-diamine	95-80-7
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
2,4,6-Trichlorophenol	88-06-2
2,4,5-Trichlorophenol	95-95-4
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	93-76-5
2,4,5-Trichlorophenoxypropionic acid (2,4,5-TP)	93-72-1
Warfarin	81-81-2

[a] Chemical Abstract Services Registry Number.

Table 1 presents average percent recovery and percent RSD data for these analytes, as well as the retention volumes of each analyte on a single GPC system. Retention volumes vary from column to column. Figure 1 provides additional information on retention volumes for certain classes of compounds. The data for the semivolatiles were determined by GC/MS, whereas, the pesticide data were determined by GC/ECD or GC/FPD. Compounds not amenable to GC were determined by HPLC. Other analytes may also be appropriate for this cleanup technique, however, recovery through the GPC should be >70%.

1.4 Normally, this method is most efficient for removing high boiling materials that condense in the injection port area of a gas chromatograph (GC) or the front of the GC column. This residue will ultimately reduce the chromatographic separation efficiency or column capacity because of adsorption of the target analytes on the active sites. Pentachlorophenol is especially susceptible to this problem. GPC, operating on the principal of size exclusion, will not usually remove interference peaks that appear in the chromatogram since the molecular size of these compounds is relative similar to the target analytes. Separation cleanup techniques, based on other molecular characteristics (i.e., polarity), must be used to eliminate this type of interference.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required amount of preswelled absorbent, and is flushed with solvent for an extended period. The column is calibrated and then loaded with the sample extract to be cleaned up. Elution is effected with a suitable solvent(s) and the product is then concentrated.

3.0 INTERFERENCES

3.1 A reagent blank should be analyzed for the compound of interest prior to the use of this method. The level of interferences must be below the estimated quantitation limits (EQLs) of the analytes of interest before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

4.0 APPARATUS

4.1 Gel-permeation chromatography system - GPC Autoprep Model 1002 A or B, or equivalent, Analytical Biochemical Laboratories, Inc. Systems that perform very satisfactorily have also been assembled from the following components - an HPLC pump, an auto sampler or a valving system with sample loops, and a fraction collector. All systems, whether automated or manual, must meet the calibration requirements of Sec. 7.2.2.

4.1.1 Chromatographic column - 700 mm x 25 mm ID glass column. Flow is upward. (Optional) To simplify switching from the UV detector during calibration to the GPC collection device during extract cleanup, attach a double 3-way valve (Rheodyne Type 50 Teflon Rotary Valve #10-262 or equivalent) so that the column exit flow can be shunted either to the UV flow-through cell or to the GPC collection device.

4.1.2 Guard column - (Optional) 5 cm, with appropriate fittings to connect to the inlet side of the analytical column (Supelco 5-8319 or equivalent).

4.1.3 Bio Beads (S-X3) - 200-400 mesh, 70 g (Bio-Rad Laboratories, Richmond, CA, Catalog 152-2750 or equivalent). An additional 5 g of Bio Beads are required if the optional guard column is employed. The quality of Bio Beads may vary from lot to lot because of excessive fines in some lots. The UV chromatogram of the Calibration solution should be very similar to that in Figure 2, and the backpressure should be within 6-10 psi. Also, the gel swell ratio in methylene chloride should be in the range of 4.4 - 4.8 mL/g. In addition to fines having a detrimental effect on chromatography, they can also pass through the column screens and damage the valve.

4.1.4 Ultraviolet detector - Fixed wavelength (254 nm) with a semi-prep flow-through cell.

4.1.5 Strip chart recorder, recording integrator or laboratory data system.

4.1.6 Syringe - 10 mL with Luerlok fitting.

4.1.7 Syringe filter assembly, disposable - Bio-Rad "Prep Disc" sample filter assembly #343-0005, 25 mm, and 5 micron filter discs or equivalent. Check each batch for contaminants. Rinse each filter assembly (prior to use) with methylene chloride if necessary.

4.2 Analytical balance - 0.0001 g.

4.3 Volumetric flasks, Class A - 10 mL to 1000 mL

4.4 Graduated cylinders

5.0 REAGENTS

5.1 Methylene chloride, CH_2Cl_2. Pesticide quality or equivalent.

5.1.1 Some brands of methylene chloride may contain unacceptably high levels of acid (HCl). Check the pH by shaking equal portions of methylene chloride and water, then check the pH of the water layer.

5.1.1.1 If the pH of the water layer is $\leq$ 5, filter the entire supply of solvent through a 2 in. x 15 in. glass column containing activated basic alumina. This column should be sufficient for processing approximately 20-30 liters of solvent. Alternatively, find a different supply of methylene chloride.

5.2 Cyclohexane, C_6H_{12}. Pesticide quality or equivalent.

5.3 n-Butyl chloride, $CH_3CH_2CH_2CH_2Cl$. Pesticide quality or equivalent.

5.4 GPC Calibration Solution. Prepare a calibration solution in methylene chloride containing the following analytes (in elution order):

Compound	mg/L
corn oil	25,000
bis(2-ethylhexyl) phthalate	1,000
methoxychlor	200
perylene	20
sulfur	80

NOTE: Sulfur is not very soluble in methylene chloride, however, it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds.

Store the calibration solution in an amber glass bottle with a Teflon lined screw-cap at 4°C, and protect from light. (Refrigeration may cause the corn oil to precipitate. Before use, allow the calibration solution to stand at room temperature until the corn oil dissolves.) Replace the calibration standard solution every 6 months, or more frequently if necessary.

5.5 Corn Oil Spike for Gravimetric Screen. Prepare a solution of corn oil in methylene chloride (5 g/100 mL).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 It is very important to have consistent laboratory temperatures during an entire GPC run, which could be 24 hours or more. If temperatures are not consistent, retention times will shift, and the dump and collect times determined by the calibration standard will no longer be appropriate. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 72°F.

7.2 GPC Setup and Calibration

7.2.1 Column Preparation

7.2.1.1 Weigh out 70 g of Bio Beads (SX-3). Transfer them to a quart bottle with a Teflon lined cap or a 500 mL separatory funnel with a large bore stopcock, and add approximately 300 mL of methylene chloride. Swirl the container to ensure the wetting of all beads. Allow the beads to swell for a minimum of 2 hours. Maintain enough solvent to sufficiently cover the beads at all times. If a guard column is to be used, repeat the above with 5 g of Bio Beads in a 125 mL bottle or a beaker, using 25 mL of methylene chloride.

7.2.1.2 Turn the column upside down from its normal position, and remove the inlet bed support plunger (the inlet plunger is longer than the outlet plunger). Position and tighten the outlet bed support plunger as near the end as possible, but no closer than 5 cm (measured from the gel packing to the collar).

7.2.1.3 Raise the end of the outlet tube to keep the solvent in the GPC column, or close the column outlet stopcock if one is attached. Place a small amount of solvent in the column to minimize the formation of air bubbles at the base of poured column packing.

7.2.1.4 Swirl the bead/solvent slurry to get a homogeneous mixture and, if the wetting was done in a quart bottle, quickly transfer it to a 500 mL separatory funnel with a large bore stopcock. Drain the excess methylene chloride directly into the waste beaker, and then start draining the slurry into the column by placing the separatory funnel tip against the column wall. This will help to minimize bubble formation. Swirl occasionally to keep the slurry homogeneous. Drain enough to fill the column. Place the tubing from the column outlet into a waste beaker below the column, open the stopcock (if attached) and allow the excess solvent to drain. Raise the tube to stop the flow and close the stopcock when the top of the gel begins to look dry. Add additional methylene chloride to just rewet the gel.

7.2.1.5 Wipe any remaining beads and solvent from the inner walls of the top of the column with a laboratory tissue. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make the seal just tight

enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

CAUTION: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

7.2.1.6 Compress the column as much as possible without applying excessive force. Loosen the seal and gradually pull out the plunger. Rinse and wipe off the plunger. Slurry any remaining beads and transfer them into the column. Repeat Sec. 7.2.1.5 and reinsert the plunger. If the plunger cannot be inserted and pushed in without allowing beads to escape around the seal, continue compression of the beads without tightening the seal, and loosen and remove the plunger as described. Repeat this procedure until the plunger is successfully inserted.

7.2.1.7 Push the plunger until it meets the gel, then compress the column bed about four centimeters.

7.2.1.8 Pack the optional 5 cm column with approximately 5 g of preswelled beads (different guard columns may require different amounts). Connect the guard column to the inlet of the analytical column.

7.2.1.9 Connect the column inlet to the solvent reservoir (reservoir should be placed higher than the top of the column) and place the column outlet tube in a waste container. Placing a restrictor in the outlet tube will force air out of the column more quickly. A restrictor can be made from a piece of capillary stainless steel tubing of 1/16" OD x 10/1000" ID x 2". Pump methylene chloride through the column at a rate of 5 mL/min for one hour.

7.2.1.10 After washing the column for at least one hour, connect the column outlet tube, without the restrictor, to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. A restrictor (same size as in Sec. 7.2.1.9) in the outlet tube from the UV detector will prevent bubble formation which causes a noisy UV baseline. The restrictor will not effect flow rate. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until approximately 6-10 psi backpressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

7.2.1.11 When the GPC column is not to be used for several days, connect the column outlet line to the column inlet to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, reswelled, and repoured as described above. If drying occurs, methylene chloride should be pumped through the column until the observed column pressure is constant and the column appears wet. Always recalibrate after column drying has occurred to verify retention volumes have not changed.

7.2.2 Calibration of the GPC Column

7.2.2.1 Using a 10 mL syringe, load sample loop #1 with calibration solution (Sec. 5.6). With the ABC automated system, the 5 mL sample loop requires a minimum of 8 mL of the calibration solution. Use a firm, continuous pressure to push the sample onto the loop. Switch the valve so that GPC flow is through the UV flow-through cell.

7.2.2.2 Inject the calibration solution and obtain a UV trace showing a discrete peak for each component. Adjust the detector and/or recorder sensitivity to produce a UV trace similar to Figure 2 that meets the following requirements. Differences between manufacturers' cell volumes and detector sensitivities may require a dilution of the calibration solution to achieve similar results. An analytical flow-through detector cell will require a much less concentrated solution than the semi-prep cell, and therefore the analytical cell is not acceptable for use.

7.2.2.3 Following are criteria for evaluating the UV chromatogram for column condition.

7.2.2.3.1 Peaks must be observed, and should be symmetrical, for all compounds in the calibration solution.

7.2.2.3.2 Corn oil and phthalate peaks must exhibit >85% resolution.

7.2.2.3.3 Phthalate and methoxychlor peaks must exhibit >85% resolution.

7.2.2.3.4 Methoxychlor and perylene peaks must exhibit >85% resolution.

7.2.2.3.5 Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.

7.2.2.3.6 Nitroaromatic compounds are particularly prone to adsorption. For example, 4-nitrophenol recoveries may be low due to a portion of the analyte being discarded after the end of the collection time. Columns should be tested with the semivolatiles matrix spiking solution. GPC elution should continue until after perylene has eluted, or long enough to recover at least 85% of the analytes, whichever time is longer.

7.2.2.4 Calibration for Semivolatiles - Using the information from the UV trace, establish appropriate collect and dump time periods to ensure collection of all target analytes. Initiate column eluate collection just before elution of bis(2-ethylhexyl) phthalate and after the elution of the corn oil. Stop eluate collection shortly after the elution of perylene. Collection should be stopped before sulfur elutes. Use a "wash" time of 10 minutes after the elution of sulfur. Each laboratory is

required to establish its specific time sequences. See Figure 2 for general guidance on retention time. Figure 1 illustrates retention volumes for different classes of compounds.

7.2.2.5 Calibration for Organochlorine Pesticides/PCBs - Determine the elution times for the phthalate, methoxychlor, perylene, and sulfur. Choose a dump time which removes >85% of the phthalate, but collects >95% of the methoxychlor. Stop collection after the elution of perylene, but before sulfur elutes.

7.2.2.6 Verify the flow rate by collecting column eluate for 10 minutes in a graduated cylinder and measure the volume, which should be 45-55 mL (4.5-5.5 mL/min). If the flow rate is outside of this range, corrective action must be taken, as described above. Once the flow rate is within the range of 4.5-5.5 mL/min, record the column pressure (should be 6-10 psi) and room temperature. Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times, and must be monitored. If the flow rate and/or column pressure do not fall within the above ranges, a new column should be prepared. A UV trace that does not meet the criteria in Sec. 7.2.2.3 would also indicate that a new column should be prepared. It may be necessary to obtain a new lot of Bio Beads if the column fails all the criteria.

7.2.2.7 Reinject the calibration solution after appropriate collect and dump cycles have been set, and the solvent flow and column pressure have been established.

7.2.2.7.1 Measure and record the volume of collected GPC eluate in a graduated cylinder. The volume of GPC eluate collected for each sample extract processed may be used to indicate problems with the system during sample processing.

7.2.2.7.2 The retention times for bis(2-ethylhexyl) phthalate and perylene must not vary more than ±5% between calibrations. If the retention time shift is >5%, take corrective action. Excessive retention time shifts are caused by:

7.2.2.7.2.1 Poor laboratory temperature control or system leaks.

7.2.2.7.2.2 An unstabilized column that requires pumping methylene chloride through it for several more hours or overnight.

7.2.2.7.2.3 Excessive laboratory temperatures, causing outgassing of the methylene chloride.

7.2.2.8 Analyze a GPC blank by loading 5 mL of methylene chloride into the GPC. Concentrate the methylene chloride that passes through the system during the collect cycle using a Kuderna-Danish (KD) evaporator. Analyze the concentrate by whatever detectors will be used for the analysis of future samples. Exchange

the solvent, if necessary. If the blank exceeds the estimated quantitation limit of the analytes, pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank to ensure the system is sufficiently clean. Repeat the methylene chloride pumping, if necessary.

7.3 Extract Preparation

7.3.1 Adjust the extract volume to 10.0 mL. The solvent extract must be primarily methylene chloride. All other solvents, e.g. 1:1 methylene chloride/acetone, must be concentrated to 1 mL (or as low as possible if a precipitate forms) and diluted to 10.0 mL with methylene chloride. Thoroughly mix the extract before proceeding.

7.3.2 Filter the extract through a 5 micron filter disc by attaching a syringe filter assembly containing the filter disc to a 10 mL syringe. Draw the sample extract through the filter assembly and into the 10 mL syringe. Disconnect the filter assembly before transferring the sample extract into a small glass container, e.g. a 15 mL culture tube with a Teflon lined screw cap. Alternatively, draw the extract into the syringe without the filter assembly. Attach the filter assembly and force the extract through the filter and into the glass container. The latter is the preferred technique for viscous extracts or extracts with a lot of solids. Particulate larger than 5 microns may scratch the valve, which may result in a system leak and cross-contamination of sample extracts in the sample loops. Repair of the damaged valve is quite expensive.

NOTE: Viscosity of a sample extract should not exceed the viscosity of 1:1 water/glycerol. Dilute samples that exceed this viscosity.

7.4 Screening the Extract

7.4.1 Screen the extract to determine the weight of dissolved residue by evaporating a 100 µL aliquot to dryness and weighing the residue. The weight of dissolved residue loaded on the GPC column cannot exceed 0.500 g. Residues exceeding 0.500 g will very likely result in incomplete extract cleanup and contamination of the GPC switching valve (which results in cross-contamination of sample extracts).

7.4.1.1 Transfer 100 µL of the filtered extract from Sec. 7.3.2 to a tared aluminum weighing dish.

7.4.1.2 A suggested evaporation technique is to use a heat lamp. Set up a 250 watt heat lamp in a hood so that it is 8 ± 0.5 cm from a surface covered with a clean sheet of aluminum foil. Surface temperature should be 80-100°C (check temperature by placing a thermometer on the foil and under the lamp). Place the weighing dish under the lamp using tongs. Allow it to stay under the lamp for 1 min. Transfer the weighing dish to an analytical balance or a micro balance and weigh to the nearest 0.1 mg. If the residue weight is less than 10 mg/100 µL, then further weighings are not necessary. If the residue weight is greater than 10 mg/100 µL,

then determine if constant weight has been achieved by placing the weighing dish and residue back under the heat lamp for 2 or more additional 0.5 min. intervals. Reweigh after each interval. Constant weight is achieved when three weights agree within ±10%.

7.4.1.3 Repeat the above residue analysis on a blank and a spike. Add 100 µL of the same methylene chloride used for the sample extraction to a weighing dish and determine residue as above. Add 100 µL of a corn oil spike (5 g/100 mL) to another weighing dish and repeat the residue determination.

7.4.2 A residue weight of 10 mg/100 µL of extract represents 500 mg in 5 mL of extract. Any sample extracts that exceed the 10 mg/100 µL residue weight must be diluted so that the 5 mL loaded on the GPC column does not exceed 0.500 g. When making the dilution, keep in mind that a minimum volume of 8 mL is required when loading the ABC GPC unit. Following is a calculation that may be used to determine what dilution is necessary if the residue exceeds 10 mg.

$$\text{Y mL taken for dilution} = \text{10 mL final volume} \times \frac{\text{10 mg maximum}}{\text{X mg of residue}}$$

Example:

$$\text{Y mL taken for dilution} = \text{10 mL final volume} \times \frac{\text{10 mg maximum}}{\text{15 mg of residue}}$$

Y mL taken for dilution = 6.7 mL

Therefore, taking 6.7 mL of sample extract from Sec. 7.3.2, and diluting to 10 mL with methylene chloride, will result in 5 mL of diluted extract loaded on the GPC column that contains 0.500 g of residue.

NOTE: This dilution factor must be included in the final calculation of analyte concentrations. In the above example, the dilution factor is 1.5.

7.5 GPC Cleanup

7.5.1 Calibrate the GPC at least once per week following the procedure outlined in Secs. 7.2.2 through 7.2.2.6. Ensure that UV trace requirements, flow rate and column pressure criteria are acceptable. Also, the retention time shift must be <5% when compared to retention times in the last calibration UV trace.

7.5.1.1 If these criteria are not met, try cleaning the column by loading one or more 5 mL portions of butyl chloride and running it through the column. Butyl chloride or 9:1 (v/v) methylene chloride/methanol removes the discoloration and particulate that may have precipitated out of the methylene chloride extracts. Backflushing (reverse flow) with methylene chloride to dislodge particulates may restore lost resolution. If a guard column is being used, replace it with a new one. This may correct

the problem. If column maintenance does not restore acceptable performance, the column must be repacked with new Bio Beads and calibrated.

7.5.2 Draw a minimum of 8 mL of extract (diluted, if necessary, and filtered) into a 10 mL syringe.

7.5.3 Attach the syringe to the turn lock on the injection port. Use firm, continuous pressure to push the sample onto the 5-mL sample loop. If the sample is difficult to load, some part of the system may be blocked. Take appropriate corrective action. If the back pressure is normal (6-10 psi), the blockage is probably in the valve. Blockage may be flushed out of the valve by reversing the inlet and outlet tubes and pumping solvent through the tubes. (This should be done before sample loading.)

NOTE: Approximately 2 mL of the extract remains in the lines between the injection port and the sample loop; excess sample also passes through the sample loop to waste.

7.5.4 After loading a loop, and before removing the syringe from the injection port, index the GPC to the next loop. This will prevent loss of sample caused by unequal pressure in the loops.

7.5.5 After loading each sample loop, wash the loading port with methylene chloride in a PTFE wash bottle to minimize cross-contamination. Inject approximately 10 mL of methylene chloride to rinse the common tubes.

7.5.6 After loading all the sample loops, index the GPC to the 00 position, switch to the "RUN" mode and start the automated sequence. Process each sample using the collect and dump cycle times established in Sec. 7.2.2.

7.5.7 Collect each sample in a 250 mL Erlenmeyer flask, covered with aluminum foil to reduce solvent evaporation, or directly into a Kuderna-Danish evaporator. Monitor sample volumes collected. Changes in sample volumes collected may indicate one or more of the following problems:

7.5.7.1 Change in solvent flow rate, caused by channeling in the column or changes in column pressure.

7.5.7.2 Increase in column operating pressure due to the absorption of particles or gel fines onto either the guard column or the analytical column gel, if a guard column is not used.

7.5.7.3 Leaks in the system or significant variances in room temperature.

7.6 Concentrate the extract by the standard K-D technique (see any of the extraction methods, Sec. 4.2.1 of this chapter). See the determinative methods (Chapter Four, Sec. 4.3) for the final volume.

7.7 It should be remembered that only half of the sample extract is processed by the GPC (5 mL of the 10 mL extract is loaded onto the GPC column), and thus, a dilution factor of 2 (or 2 multiplied by any dilution factor in Sec. 7.4.2) must be used for quantitation of the sample in the determinative method.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 3600 for specific quality control procedures.

8.2 The analyst should demonstrate that the compound(s) of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Refer to Table 1 for single laboratory performance data.

10.0 REFERENCES

1. Wise, R.H.; Bishop, D.F.; Williams, R.T.; Austern, B.M. "Gel Permeation Chromatography in the GC/MS Analysis of Organics in Sludges"; U.S. EPA Municipal Environmental Research Laboratory: Cincinnati, Ohio 45268.

2. Czuczwa, J.; Alford-Stevens, A. "Optimized Gel Permeation Chromatographic Cleanup for Soil, Sediment, Waste and Waste Oil Sample Extracts for GC/MS Determination of Semivolatile Organic Pollutants, JAOAC, submitted April 1989.

3. Marsden, P.J.; Taylor, V.; Kennedy, M.R. "Evaluation of Method 3640 Gel Permeation Cleanup"; Contract No. 68-03-3375, U.S. Environmental Protection Agency, Cincinnati, Ohio, pp. 100, 1987.

TABLE 1
GPC RECOVERY AND RETENTION VOLUMES FOR RCRA
APPENDIX VIII ANALYTES

Compound	% Rec[1]	% RSD[2]	Ret. Vol.[3] (mL)
Acenaphthene	97	2	196-235
Acenaphthylene	72	10	196-235
Acetophenone	94	7	176-215
2-Acetylaminofluorene	97	2	156-195
Aldrin	99	9	196-215
4-Aminobiphenyl	96	7	176-215
Aniline	93	4	196-235
Anthracene	89	2	196-235
Benomyl	131	8	146-195
Benzenethiol	92	11	196-235
Benzidine	95	5	176-215
Benz(a)anthracene	100	3	196-235
Benzo(b)fluoranthene	93	5	196-235
Benzo(a)pyrene	93	3	196-235
Benzo(ghi)perylene	90	6	196-235
Benzo(k)fluoranthene	91	4	196-235
Benzoic acid	66	7	176-195
Benzotrichloride	93	7	176-215
Benzyl alcohol	95	17	176-215
Benzyl chloride	99	4	176-215
alpha-BHC	84	13	196-215
beta-BHC	94	9	196-215
gamma-BHC	93	4	196-215
delta-BHC	102	7	216-255
4-Bromophenyl phenyl ether	93	1	176-215
Butyl benzyl phthalate	104	3	136-175
2-sec-butyl-4,6-dinitrophenol (Dinoseb)	103	18	176-195
Carbazole	99	5	196-255
Carbendazim	131	8	146-195
alpha-Chlordane	97	2	196-235
gamma-Chlordane	93	2	196-215
4-Chloro-3-methylphenol	87	1	196-255
4-Chloroaniline	88	3	196-235
Chlorobenzilate	92	5	176-235
Bis(2-chloroethoxy)methane	89	1	156-195
Bis(2-chloroethyl) ether	76	2	156-215
Bis(2-chloroisopropyl) ether	83	2	156-195
2-Chloronaphthalene	89	1	196-235
2-Chlorophenol	90	1	196-215
3-Chlorophenol	86	3	196-215
4-Chlorophenol	87	2	196-215
4-Chlorophenyl phenyl ether	98	2	176-215
3-Chloropropionitrile	80	5	176-215
Chrysene	102	1	196-235
2-Cresol	91	1	196-215

TABLE 1 (continued)

Compound	% Rec[1]	%RSD[2]	Ret. Vol.[3] (mL)
3-Cresol	70	3	196-215
4-Cresol	88	2	196-215
Cyclophosphamide	114	10	146-185
DDD	94	4	196-235
DDE	94	2	196-235
DDT	96	6	176-215
Di-n-butyl phthalate	104	3	136-175
Diallate	97	6	156-175
Dibenzo(a,e)pyrene	94	10	216-235
Dibenzo(a,i)pyrene	99	8	216-235
Dibenz(a,j)acridine	117	9	176-195
Dibenz(a,h)anthracene	92	5	196-235
Dibenzofuran	94	1	176-235
Dibenzothiophene	94	3	196-235
1,2-Dibromo-3-chloropropane	83	2	176-215
1,2-Dibromoethane	121	8	196-215
trans-1,4-Dichloro-2-butene	107	6	176-195
cis-1,4-Dichloro-2-butene	106	6	176-215
1,2-Dichlorobenzene	81	1	196-235
1,3-Dichlorobenzene	81	1	196-235
1,4-Dichlorobenzene	81	1	196-235
3,3′-Dichlorobenzidine	98	3	176-215
2,6-Dichlorophenol	86	3	196-215
2,4-Dichlorophenoxyacetic acid (2,4-D)	80	NA	76-215
2,4-Dichlorophenol	87	2	96-215
2,4-Dichlorotoluene	70	9	196-235
1,3-Dichloro-2-propanol	73	13	176-215
Dieldrin	100	5	196-215
Diethyl phthalate	103	3	136-195
Dimethoate	79	15	146-185
3,3′-Dimethoxybenzidine[a]	15	11	156-195
Dimethyl phthalate	100	1	156-195
p-Dimethylaminoazobenzene	96	1	176-215
7,12-Dimethyl-benz(a)anthracene	77	1	176-215
2,4-Dimethylphenol	93	2	176-215
3,3′-Dimethylbenzidine	93	2	156-215
4,6-Dinitro-o-cresol	100	1	156-195
1,3-Dinitrobenzene	99	2	156-195
2,4-Dinitrophenol	118	7	176-195
2,4-Dinitrotoluene	93	4	156-195
2,6-Dinitrotoluene	101	2	156-175
Diphenylamine	95	6	176-235
Diphenyl ether	67	12	196-215
1,2-Diphenylhydrazine	92	1	176-215
Disulfoton	81	15	146-165
Endosulfan sulfate	94	2	176-195
Endosulfan I	99	8	176-215

TABLE 1 (continued)

Compound	% Rec[1]	%RSD[2]	Ret. Vol.[3] (mL)
Endosulfan II	92	6	196-215
Endrin	95	6	196-215
Endrin aldehyde	97	1	176-215
Endrin ketone	94	4	176-215
Ethyl methane sulfonate	62	7	176-235
Ethyl methacrylate	126	7	176-195
Bis(2-ethylhexyl) phthalate	101	1	120-145
Famphur	99	NA	126-165
Fluorene	95	1	176-235
Fluoranthene	94	1	196-235
Heptachlor	85	2	195-215
Heptachlor epoxide	91	11	156-195
Hexachlorobenzene	108	2	196-235
Hexachlorobutadiene	86	2	176-215
Hexachlorocyclopentadiene	89	3	176-215
Hexachloroethane	85	1	196-235
Hexachloropropene	91	2	196-235
Indeno(1,2,3-cd)pyrene	79	13	216-255
Isodrin	98	5	196-235
Isophorone	68	7	156-195
cis-Isosafrole	90	4	176-215
trans-Isosafrole	88	16	156-195
Kepone	102	NA	196-235
Malononitrile	111	9	156-195
Merphos	93	12	126-165
Methoxychlor	94	6	156-195
3-Methylcholanthrene	74	12	176-195
2-Methylnaphthalene	67	6	196-215
Methyl parathion	84	13	146-185
4,4′-Methylene-bis(2-chloroaniline)	96	1	176-215
Naphthalene	95	7	196-215
1,4-Naphthoquinone	73	7	176-215
2-Naphthylamine	94	8	196-235
1-Naphthylamine	96	6	196-235
5-Nitro-o-toluidine	77	2	176-195
2-Nitroaniline	96	8	176-215
3-Nitroaniline	96	2	176-215
4-Nitroaniline	103	8	176-215
Nitrobenzene	86	2	176-195
2-Nitrophenol	95	3	176-195
4-Nitrophenol	77	3	196-215
N-Nitroso-di-n-butylamine	89	4	156-175
N-Nitrosodiethanolamine	104	3	146-185
N-Nitrosodiethylamine	94	2	156-175
N-Nitrosodimethylamine	86	13	156-195
N-Nitrosodiphenylamine	99	2	156-195
N-Nitrosodi-n-propylamine	85	4	156-175

TABLE 1 (continued)

Compound	% Rec[1]	%RSD[2]	Ret. Vol.[3] (mL)
N-Nitrosomethylethylamine	83	7	156-175
N-Nitrosomorpholine	86	4	156-195
N-Nitrosopiperidine	84	4	156-195
N-Nitrosopyrolidine	92	1	156-175
Di-n-octyl phthalate	83	4	120-156
Parathion	109	14	146-170
Pentachlorobenzene	95	2	196-235
Pentachloroethane	74	1	196-235
Pentachloronitrobenzene (PCNB)	91	8	156-195
Pentachlorophenol	102	1	196-215
Phenacetin	100	3	156-195
Phenanthrene	94	2	196-235
Phenol	83	2	156-195
1,2-Phenylenediamine	91	1	196-215
Phorate	74	NA	116-135
2-Picoline	99	14	156-215
Pronamide	105	15	156-195
Pyrene	98	2	215-235
Resorcinol	70	6	196-215
Safrole	93	1	176-215
Streptozotocin[a]	6	48	225-245
1,2,4,5-Tetrachlorobenzene	96	2	196-235
2,3,5,6-Tetrachloro-nitrobenzene	85	9	176-215
2,3,4,6-Tetrachlorophenol	95	1	196-215
2,3,5,6-Tetrachlorophenol	96	7	196-215
Tetraethyl dithiopyrophosphate (Sulfotep)	89	14	116-135
Thiosemicarbazide	74	3	146-185
2-Toluidine	92	3	176-235
4-Toluidine	87	8	176-235
Thiourea, 1-(o-chlorophenyl)	75	11	166-185
Toluene-2,4-diamine	69	7	176-215
1,2,3-Trichlorobenzene	87	1	196-235
1,2,4-Trichlorobenzene	89	1	196-235
2,4,5-Trichlorophenol	77	1	216-235
2,4,6-Trichlorophenol	95	1	216-235
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	71	23	156-235
2,4,5-Trichlorophenoxypropionic acid	67	NA	216-215
Warfarin	94	2	166-185

NA = Not applicable, recovery presented as the average of two determinations.

[a] Not an appropriate analyte for this method.

[1] The percent recovery is based on an average of three recovery values.

[2] The % relative standard deviation is determined from three recovery values.

[3] These Retention Volumes are for guidance only as they will differ from column to column and from system to system.

Figure 1
GPC RETENTION VOLUME OF CLASSES OF ANALYTES

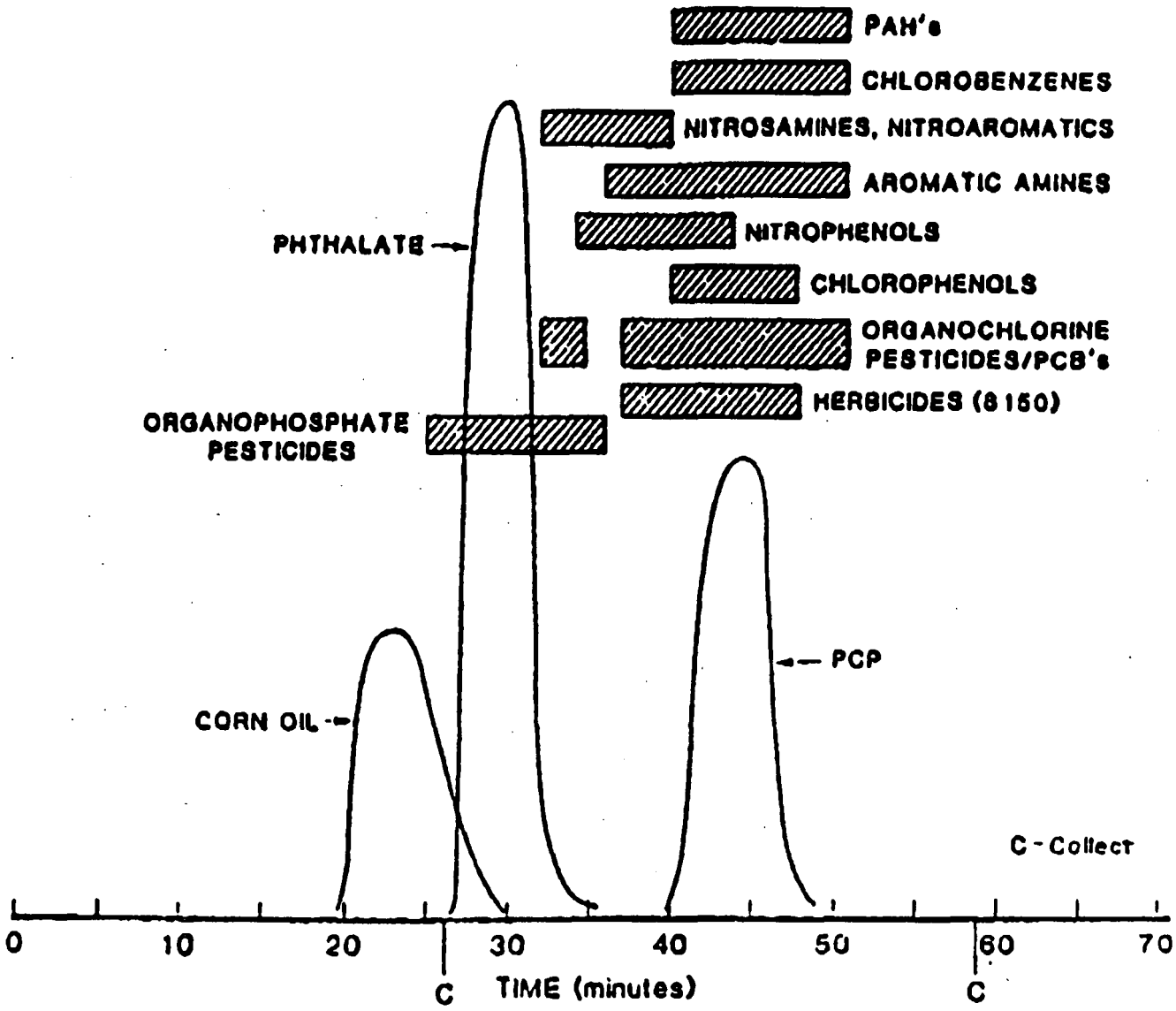
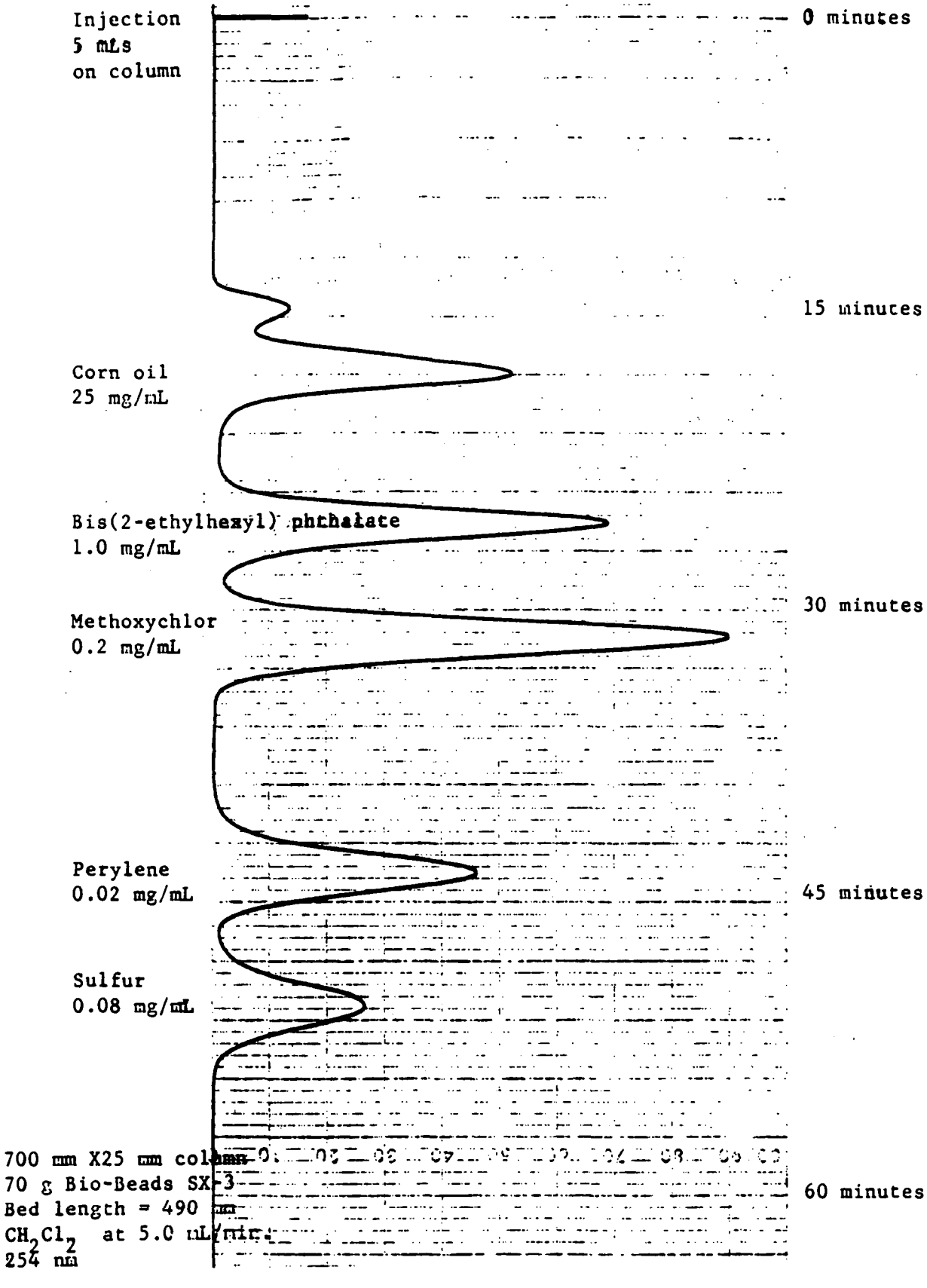
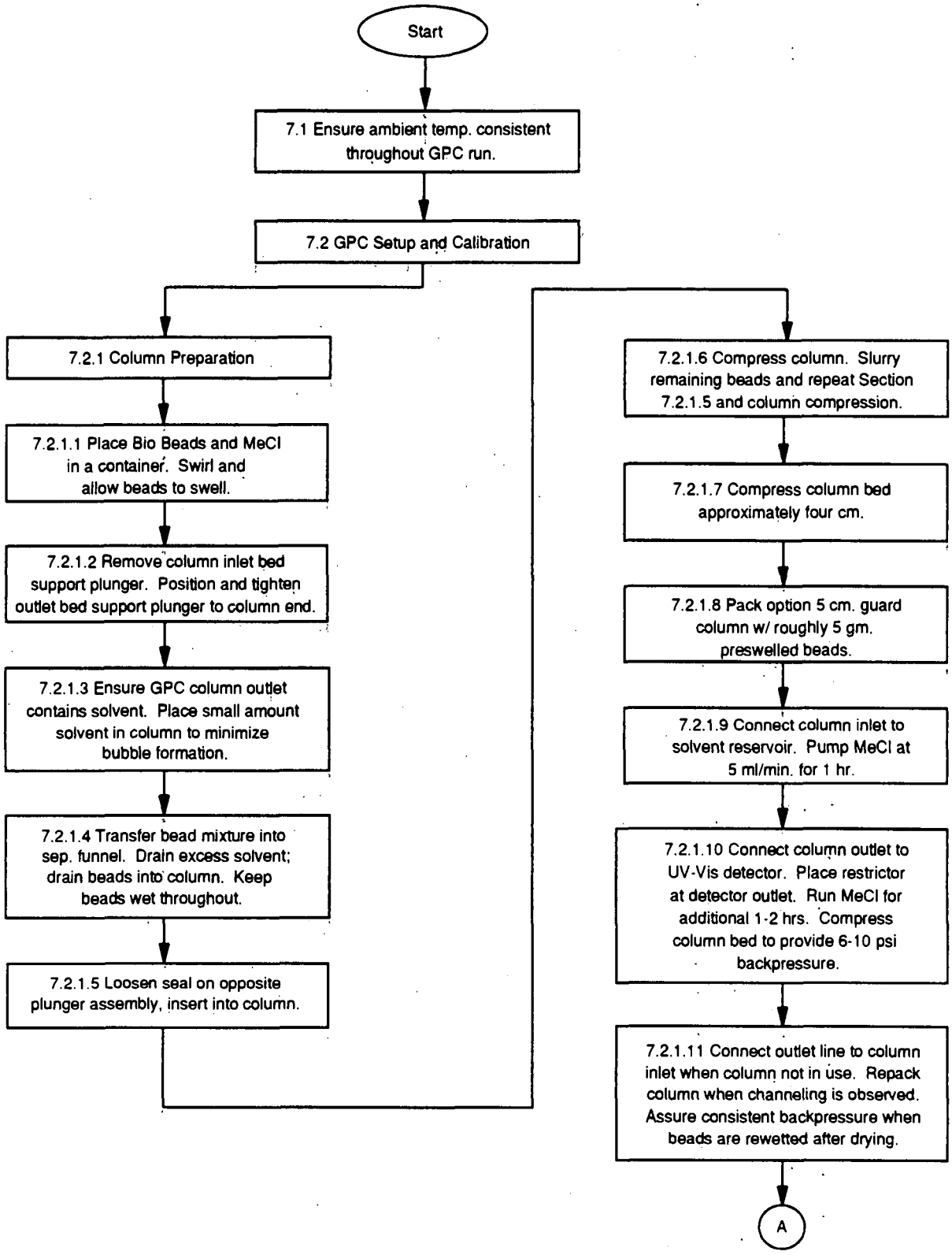
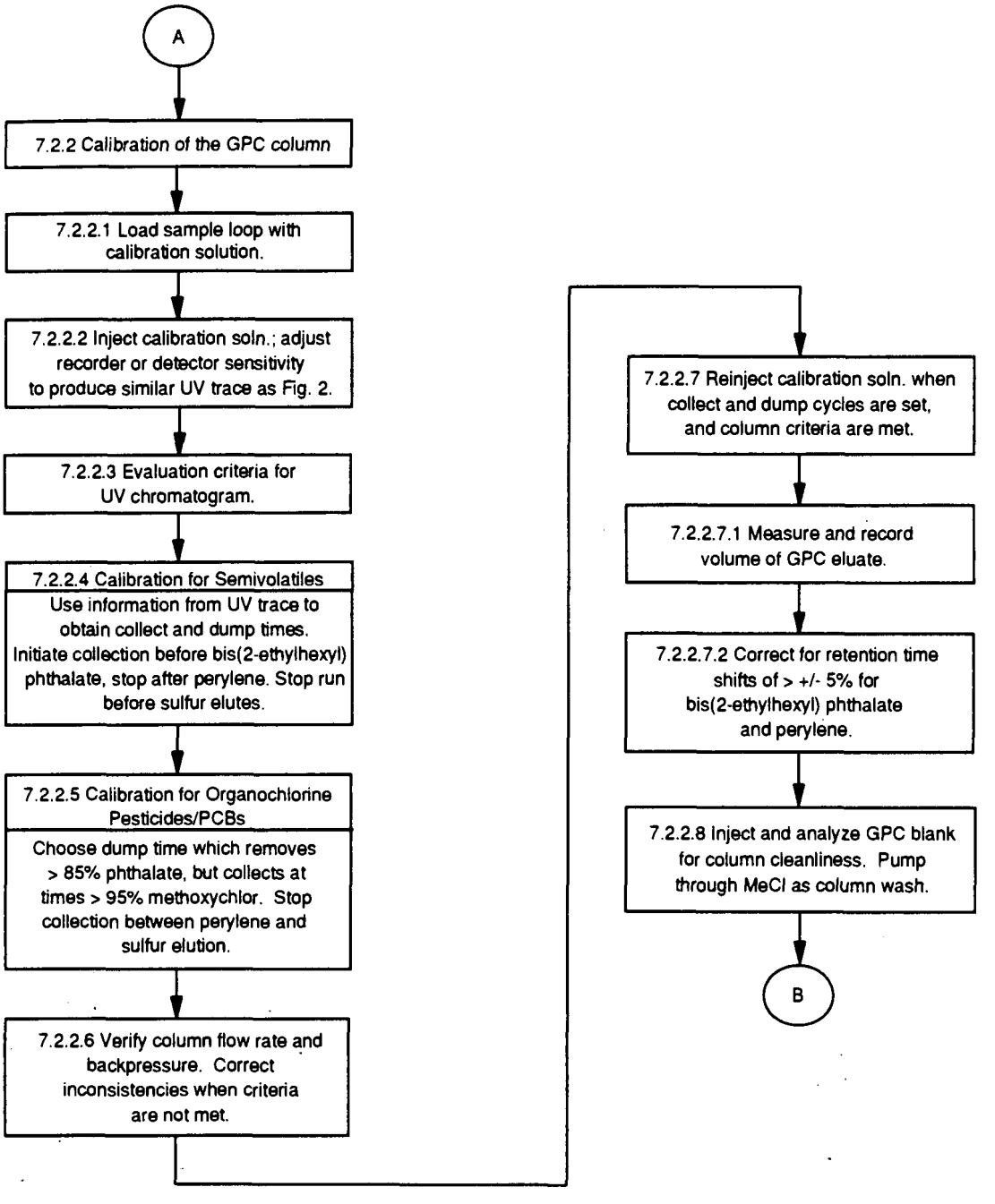
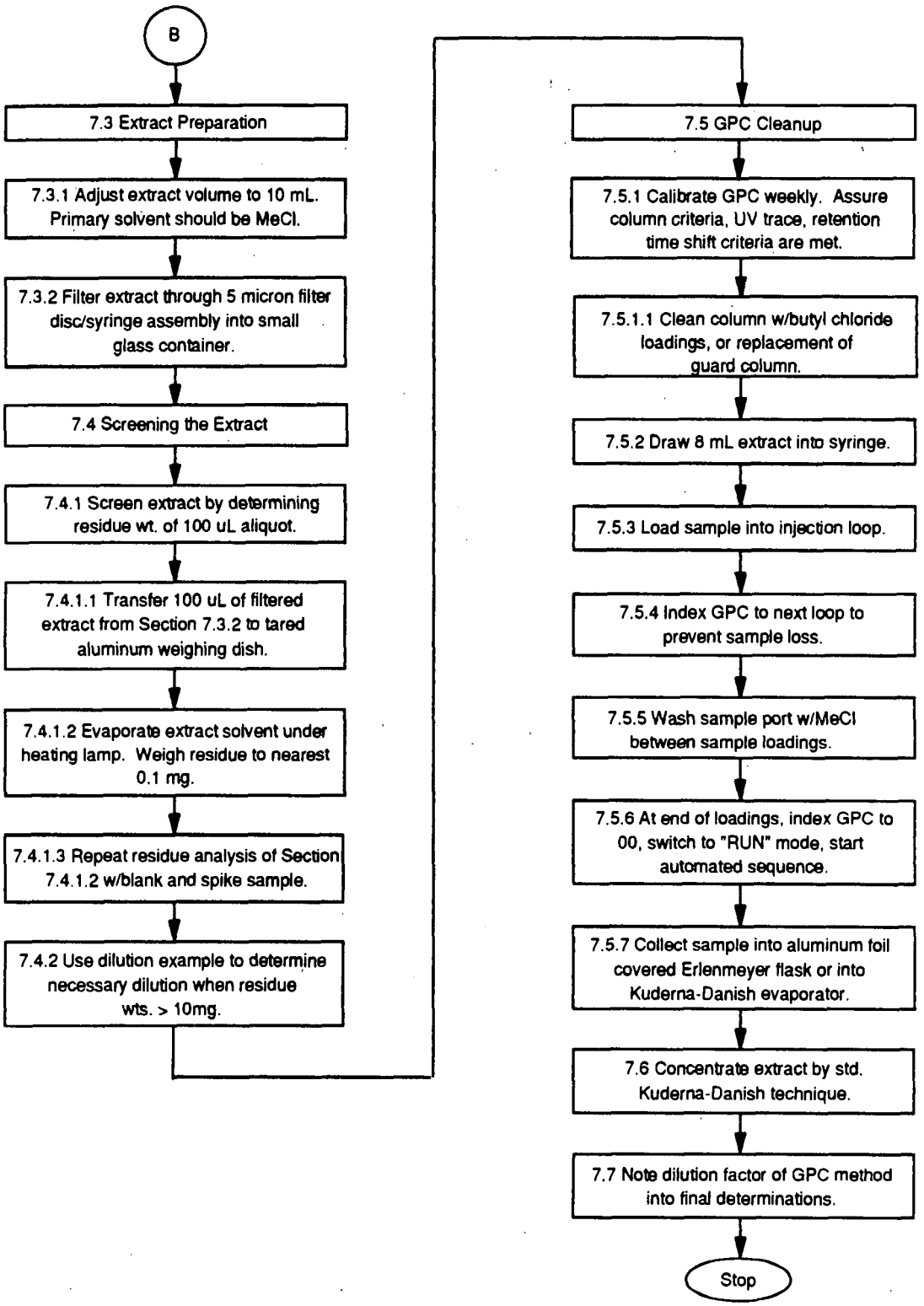


Figure 2
UV CHROMATOGRAM OF THE CALIBRATION SOLUTION




Start
7.1 Ensure ambient temp. consistent throughout GPC run.
7.2 GPC Setup and Calibration
7.2.1 Column Preparation
7.2.1.1 Place Bio Beads and MeCl in a container. Swirl and allow beads to swell.
7.2.1.2 Remove column inlet bed support plunger. Position and tighten outlet bed support plunger to column end.
7.2.1.3 Ensure GPC column outlet contains solvent. Place small amount solvent in column to minimize bubble formation.
7.2.1.4 Transfer bead mixture into sep. funnel. Drain excess solvent; drain beads into column. Keep beads wet throughout.
7.2.1.5 Loosen seal on opposite plunger assembly, insert into column.
7.2.1.6 Compress column. Slurry remaining beads and repeat Section 7.2.1.5 and column compression.
7.2.1.7 Compress column bed approximately four cm.
7.2.1.8 Pack option 5 cm. guard column w/ roughly 5 gm. preswelled beads.
7.2.1.9 Connect column inlet to solvent reservoir. Pump MeCl at 5 ml/min. for 1 hr.
7.2.1.10 Connect column outlet to UV-Vis detector. Place restrictor at detector outlet. Run MeCl for additional 1-2 hrs. Compress column bed to provide 6-10 psi backpressure.
7.2.1.11 Connect outlet line to column inlet when column not in use. Repack column when channeling is observed. Assure consistent backpressure when beads are rewetted after drying.
A


A
7.2.2 Calibration of the GPC column
7.2.2.1 Load sample loop with calibration solution.
7.2.2.2 Inject calibration soln.; adjust recorder or detector sensitivity to produce similar UV trace as Fig. 2.
7.2.2.3 Evaluation criteria for UV chromatogram.
7.2.2.4 Calibration for Semivolatiles
Use information from UV trace to obtain collect and dump times. Initiate collection before bis(2-ethylhexyl) phthalate, stop after perylene. Stop run before sulfur elutes.
7.2.2.5 Calibration for Organochlorine Pesticides/PCBs
Choose dump time which removes > 85% phthalate, but collects at times > 95% methoxychlor. Stop collection between perylene and sulfur elution.
7.2.2.6 Verify column flow rate and backpressure. Correct inconsistencies when criteria are not met.
7.2.2.7 Reinject calibration soln. when collect and dump cycles are set, and column criteria are met.
7.2.2.7.1 Measure and record volume of GPC eluate.
7.2.2.7.2 Correct for retention time shifts of > +/- 5% for bis(2-ethylhexyl) phthalate and perylene.
7.2.2.8 Inject and analyze GPC blank for column cleanliness. Pump through MeCl as column wash.
B


B
7.3 Extract Preparation
7.3.1 Adjust extract volume to 10 mL. Primary solvent should be MeCl.
7.3.2 Filter extract through 5 micron filter disc/syringe assembly into small glass container.
7.4 Screening the Extract
7.4.1 Screen extract by determining residue wt. of 100 uL aliquot.
7.4.1.1 Transfer 100 uL of filtered extract from Section 7.3.2 to tared aluminum weighing dish.
7.4.1.2 Evaporate extract solvent under heating lamp. Weigh residue to nearest 0.1 mg.
7.4.1.3 Repeat residue analysis of Section 7.4.1.2 w/blank and spike sample.
7.4.2 Use dilution example to determine necessary dilution when residue wts. > 10mg.
7.5 GPC Cleanup
7.5.1 Calibrate GPC weekly. Assure column criteria, UV trace, retention time shift criteria are met.
7.5.1.1 Clean column w/butyl chloride loadings, or replacement of guard column.
7.5.2 Draw 8 mL extract into syringe.
7.5.3 Load sample into injection loop.
7.5.4 Index GPC to next loop to prevent sample loss.
7.5.5 Wash sample port w/MeCl between sample loadings.
7.5.6 At end of loadings, index GPC to 00, switch to "RUN" mode, start automated sequence.
7.5.7 Collect sample into aluminum foil covered Erlenmeyer flask or into Kuderna-Danish evaporator.
7.6 Concentrate extract by std. Kuderna-Danish technique.
7.7 Note dilution factor of GPC method into final determinations.
Stop

METHOD 3650A

ACID-BASE PARTITION CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Method 3650 was formerly Method 3530 in the second edition of this manual.

1.2 Method 3650 is a liquid-liquid partitioning cleanup method to separate acid analytes, e.g. organic acids and phenols, from base/neutral analytes, e.g. amines, aromatic hydrocarbons, and halogenated organic compounds, using pH adjustment. It may be used for cleanup of petroleum waste prior to analysis or further cleanup (e.g., alumina cleanup). The following compounds can be separated by this method:

Compound Name	CAS No.[a]	Fraction
Benz(a)anthracene	56-55-3	Base-neutral
Benzo(a)pyrene	50-32-8	Base-neutral
Benzo(b)fluoranthene	205-99-2	Base-neutral
Chlordane	57-74-9	Base-neutral
Chlorinated dibenzodioxins		Base-neutral
2-Chlorophenol	95-57-8	Acid
Chrysene	218-01-9	Base-neutral
Creosote	8001-58-9	Base-neutral and Acid
Cresol(s)		Acid
Dichlorobenzene(s)		Base-neutral
Dichlorophenoxyacetic acid	94-75-7	Acid
2,4-Dimethylphenol	105-67-9	Acid
Dinitrobenzene	25154-54-5	Base-neutral
4,6-Dinitro-o-cresol	534-52-1	Acid
2,4-Dinitrotoluene	121-14-2	Base-neutral
Heptachlor	76-44-8	Base-neutral
Hexachlorobenzene	118-74-1	Base-neutral
Hexachlorobutadiene	87-68-3	Base-neutral
Hexachloroethane	67-72-1	Base-neutral
Hexachlorocyclopentadiene	77-47-4	Base-neutral
Naphthalene	91-20-3	Base-neutral
Nitrobenzene	98-95-3	Base-neutral
4-Nitrophenol	100-02-7	Acid
Pentachlorophenol	87-86-5	Acid
Phenol	108-95-2	Acid
Phorate	298-02-2	Base-neutral
2-Picoline	109-06-8	Base-neutral
Pyridine	110-86-1	Base-neutral
Tetrachlorobenzene(s)		Base-neutral
Tetrachlorophenol(s)		Acid
Toxaphene	8001-35-2	Base-neutral
Trichlorophenol(s)		Acid
2,4,5-TP (Silvex)	93-72-1	Acid

[a] Chemical Abstract Services Registry Number.

2.0 SUMMARY OF METHOD

2.1 The solvent extract from a prior solvent extraction method is shaken with water that is strongly basic. The acid analytes partition into the aqueous layer, whereas, the basic and neutral compounds stay in the organic solvent. The base/neutral fraction is concentrated and is then ready for further cleanup, if necessary, or analysis. The aqueous layer is acidified and extracted with an organic solvent. This extract is concentrated (if necessary) and is then ready for analysis of the acid analytes.

3.0 INTERFERENCES

3.1 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.2 A method blank must be run for the compounds of interest prior to use of the method. The interferences must be below the method detection limit before this method is applied to actual samples.

4.0 APPARATUS AND MATERIALS

4.1 Drying column - 20 mm ID Pyrex chromatographic column with Pyrex glass wool at bottom, or equivalent.

NOTE: Fritted glass discs are difficult to clean after highly contaminated extracts have been passed through them. Columns without frits are recommended. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Kuderna-Danish (K-D) apparatus

4.2.1 Concentrator tube - 10 mL graduated (Kontes K570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of the extracts.

4.2.2 Evaporation flask - 500 mL (K-570001-0500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.2.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Snyder column - Two ball micro (Kontes K569001-0219 or equivalent).

4.2.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.3 Vials - Glass, 2 mL capacity with Teflon lined screw-caps or crimp tops.

4.4 Water bath - Heated, concentric ring cover, temperature control of $\pm$ 2°C. Use this bath in a hood.

4.5 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.6 pH indicator paper - pH range including the desired extraction pH.

4.7 Separatory funnel - 125 mL.

4.8 Erlenmeyer flask - 125 mL.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium hydroxide, NaOH, (10N) - Dissolve 40 g of sodium hydroxide in 100 mL of organic-free reagent water.

5.4 Sulfuric acid, H_2SO_4, (1:1 v/v in water) - Slowly add 50 mL H_2SO_4 to 50 mL of organic-free reagent water.

5.5 Sodium sulfate (granular, anhydrous), Na_2SO_4 - Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.6 Solvents:

5.6.1 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.6.2 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.6.3 Methanol, CH_3OH - Pesticide quality or equivalent.

5.6.4 Diethyl Ether, $C_2H_5OC_2H_5$ - Pesticide quality or equivalent. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Place 10 mL of the solvent extract from a prior extraction procedure into a 125 mL separatory funnel.

7.2 Add 20 mL of methylene chloride to the separatory funnel.

7.3 Slowly add 20 mL of prechilled organic-free reagent water which has been previously adjusted to a pH of 12-13 with 10N sodium hydroxide.

7.4 Seal and shake the separatory funnel for at least 2 minutes with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to prevent unnecessary exposure of the analyst to the organic vapor.

7.5 Allow the organic layer to separate from the aqueous phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

7.6 Separate the aqueous phase and transfer it to a 125 mL Erlenmeyer flask. Repeat the extraction two more times using 20 mL aliquots of dilute sodium hydroxide (pH 12-13). Combine the aqueous extracts.

7.7 Water soluble organic acids and phenols will be primarily in the aqueous phase. Base/neutral analytes will be in the methylene chloride. If the analytes of interest are only in the aqueous phase, discard the methylene chloride and proceed to Section 7.8. If the analytes of interest are only in the methylene chloride, discard the aqueous phase and proceed to Section 7.10.

7.8 Externally cool the 125 mL Erlenmeyer flask with ice while adjusting the aqueous phase to a pH of 1-2 with sulfuric acid (1:1). Quantitatively transfer the cool aqueous phase to a clean 125 mL separatory funnel. Add 20 mL of methylene chloride to the separatory funnel and shake for at least 2 minutes. Allow the methylene chloride to separate from the aqueous phase and collect the methylene chloride in an Erlenmeyer flask.

7.9 Add 20 mL of methylene chloride to the separatory funnel and extract at pH 1-2 a second time. Perform a third extraction in the same manner combining the extracts in the Erlenmeyer flask.

7.10 Assemble a Kuderna-Danish (K-D) concentrator (if necessary) by attaching a 10 mL concentrator tube to a 500 mL evaporation flask.

7.11 Dry both acid and base/neutral fractions by passing them through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried fractions in K-D concentrators. Rinse the Erlenmeyer flasks which

contained the solvents and the columns with 20 mL of methylene chloride to complete the quantitative transfer.

7.12 Concentrate both acid and base/neutral fractions as follows: Add one or two boiling chips to the flask and attach a three ball macro-Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the warm water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to cool. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride. Concentrate the extract to the final volume using either the micro-Snyder column technique (7.12.1) or nitrogen blowdown technique (7.12.2):

7.12.1 Micro-Snyder Column Technique

7.12.1.1 Add another one or two boiling chips to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride to the top of the column. Place the K-D apparatus in a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of the liquid reaches 0.5 mL, remove the K-D apparatus and allow it to cool. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 0.2 mL of methylene chloride. Adjust the final volume to 1 mL with methylene chloride.

7.12.2 Nitrogen Blowdown Technique

7.12.2.1 Place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to 1.0-2.0 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

<u>CAUTION</u>: Do not use plasticized tubing between the carbon trap and the sample.

7.12.2.2 The internal wall of the concentrator tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the tube solvent level must be positioned to avoid condensation water. Under normal procedures, the extract must not be allowed to become dry.

<u>CAUTION</u>: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.13 The acid fraction is now ready for analysis. If the base/neutral

fraction requires further cleanup by the alumina column cleanup for petroleum waste (Method 3611), the solvent may have to be changed to hexane. If a solvent exchange is required, momentarily remove the Snyder column, add approximately 5 mL of the exchange solvent and a new boiling chip, and reattach the Snyder column. Concentrate the extract as described in Section 7.12.1.1, raising the temperature of the water bath, if necessary, to maintain proper distillation. When the apparent volume again reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Repeat the exchange 2 more times. If no further cleanup of the base/neutral extract is required, it is also ready for analysis.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for general quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst must demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

8.3 For samples that are cleaned using this method, the associated quality control samples must be processed through this cleanup method.

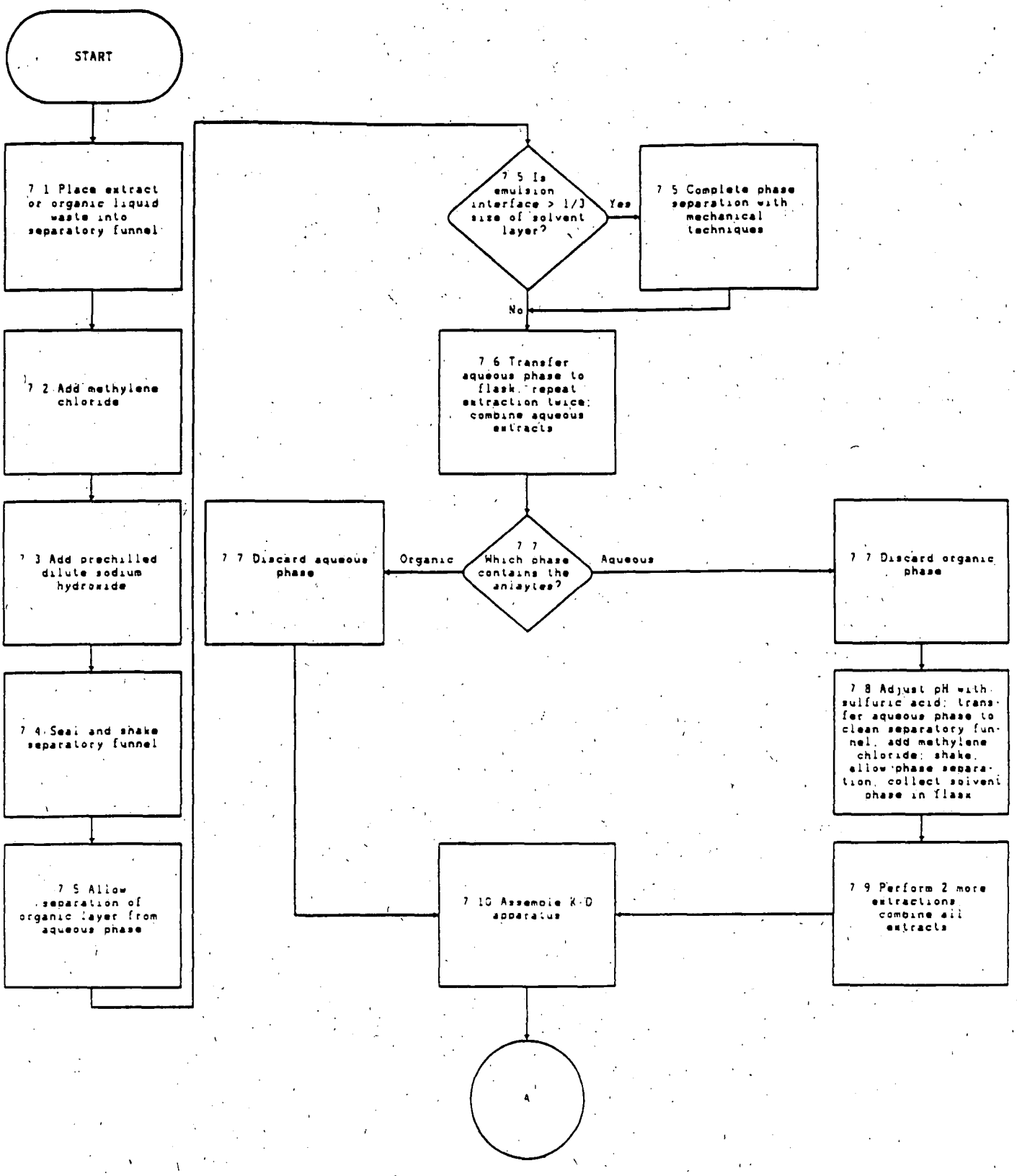
9.0 METHOD PERFORMANCE

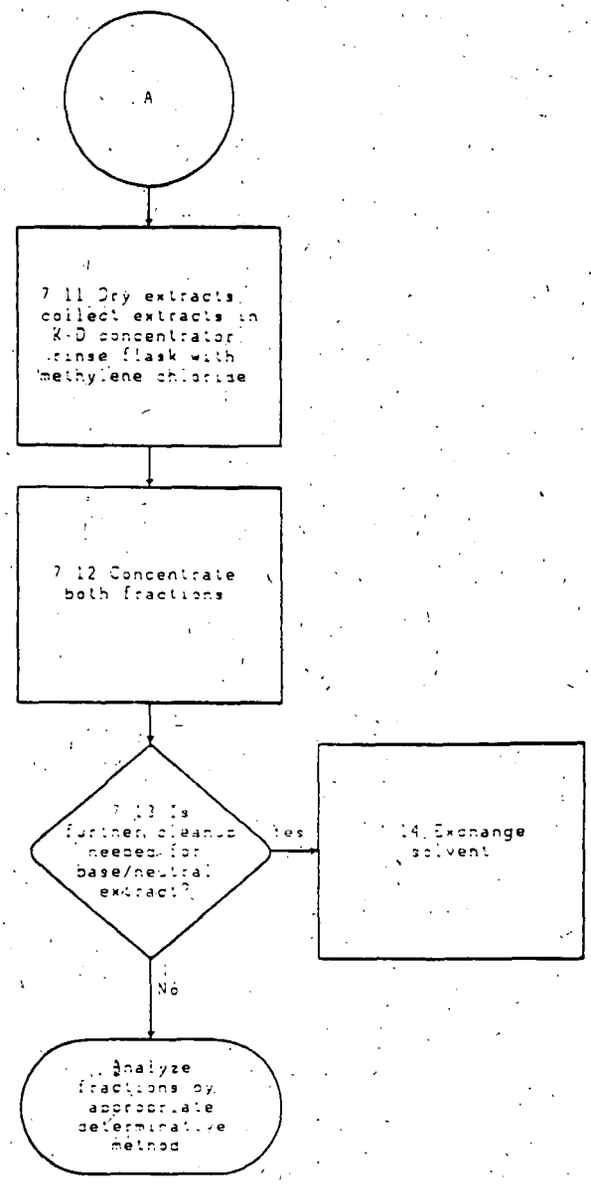
9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. Test Methods: Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1982; EPA-600/4-82-057.

METHOD 3650A
ACID-BASE PARTITION CLEANUP




A
7.11 Dry extracts, collect extracts in K-D concentrator, rinse flask with methylene chloride
7.12 Concentrate both fractions
7.13 Is further cleanup needed for base/neutral extract?
Yes
14. Exchange solvent
No
Analyze fractions by appropriate determinative method

METHOD 3660A

SULFUR CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Elemental sulfur is encountered in many sediment samples (generally specific to different areas in the country), marine algae, and some industrial wastes. The solubility of sulfur in various solvents is very similar to the organochlorine and organophosphorus pesticides. Therefore, the sulfur interference follows along with the pesticides through the normal extraction and cleanup techniques. In general, sulfur will usually elute entirely in Fraction 1 of the Florisil cleanup (Method 3620).

1.2 Sulfur will be quite evident in gas chromatograms obtained from electron capture detectors, flame photometric detectors operated in the sulfur or phosphorous mode, and Coulson electrolytic conductivity detectors in the sulfur mode. If the gas chromatograph is operated at the normal conditions for pesticide analysis, the sulfur interference can completely mask the region from the solvent peak through Aldrin.

1.3 Three techniques for the elimination of sulfur are detailed within this method: (1) the use of copper powder; (2) the use of mercury; and (3) the use of tetrabutylammonium sulfite. Tetrabutylammonium sulfite causes the least amount of degradation of a broad range of pesticides and organic compounds, while copper and mercury may degrade organophosphorus and some organochlorine pesticides.

2.0 SUMMARY OF METHOD

2.1 The sample to undergo cleanup is mixed with either copper, mercury, or tetrabutylammonium (TBA) sulfite. The mixture is shaken and the extract is removed from the sulfur cleanup reagent.

3.0 INTERFERENCES

3.1 Removal of sulfur using copper:

3.1.1 The copper must be very reactive. Therefore, all oxides of copper must be removed so that the copper has a shiny, bright appearance.

3.1.2 The sample extract must be vigorously agitated with the reactive copper for at least one minute.

4.0 APPARATUS AND MATERIALS

4.1 Mechanical shaker or mixer - Vortex Genie or equivalent.

4.2 Pipets, disposable - Pasteur type.

4.3 Centrifuge tubes, calibrated - 12 mL.

4.4 Glass bottles or vials - 10 mL and 50 mL, with Teflon-lined screw caps or crimp tops.

4.5 Kuderna-Danish (K-D) apparatus.

4.5.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.5.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.5.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.5.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.5.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Nitric acid, HNO_3, dilute.

5.4 Solvents

5.4.1 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.4.2 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.4.3 2-Propanol, $CH_3CH(OH)CH_3$ - Pesticide quality or equivalent.

5.5 Copper powder - Remove oxides by treating with dilute nitric acid, rinse with organic-free reagent water to remove all traces of acid, rinse with acetone and dry under a stream of nitrogen. (Copper, fine granular Mallinckrodt 4649 or equivalent).

5.6 Mercury, triple distilled.

5.7 Tetrabutylammonium (TBA) sulfite reagent

5.7.1 Tetrabutylammonium hydrogen sulfate, $[CH_3(CH_2)_3]_4NHSO_4$.

5.7.2 Sodium sulfite, Na_2SO_3.

5.7.3 Prepare reagent by dissolving 3.39 g tetrabutylammonium hydrogen sulfate in 100 mL organic-free reagent water. To remove impurities, extract this solution three times with 20 mL portions of hexane. Discard the hexane extracts, and add 25 g sodium sulfite to the water solution. Store the resulting solution, which is saturated with sodium sulfite, in an amber bottle with a Teflon-lined screw cap. This solution can be stored at room temperature for at least one month.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Removal of sulfur using copper

7.1.1 Concentrate the sample to exactly 1.0 mL or other known volume. Perform concentration using the Kuderna-Danish (K-D) Technique (Method 3510, Sections 7.10.1 through 7.10.4).

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.1.2 If the sulfur concentration is such that crystallization occurs, centrifuge to settle the crystals, and carefully draw off the sample extract with a disposable pipet leaving the excess sulfur in the K-D tube. Transfer 1.0 mL of the extract to a calibrated centrifuge tube.

7.1.3 Add approximately 2 g of cleaned copper powder (to the 0.5 mL mark) to the centrifuge tube. Mix for at least 1 min on the mechanical shaker.

7.1.4 Separate the extract from the copper by drawing off the extract with a disposable pipet and transfer to a clean vial. The volume remaining still represents 1.0 mL of extract.

NOTE: This separation is necessary to prevent further degradation of the pesticides.

7.2 Removal of sulfur using mercury

NOTE: Mercury is a highly toxic metal. All operations involving mercury should be performed in a hood. Prior to using mercury, it is recommended that the analyst become acquainted with proper handling and cleanup techniques associated with this metal.

7.2.1 Concentrate the sample extract to exactly 1.0 mL or other

known volume. Perform concentration using the Kuderna-Danish (K-D) Technique (Method 3510, Sections 7.10.1 through 7.10.4).

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.2.2 Pipet 1.0 mL of the extract into a clean concentrator tube or Teflon-sealed vial.

7.2.3 Add one to three drops of mercury to the vial and seal. Agitate the contents of the vial for 15-30 sec. Prolonged shaking (2 hr) may be required. If so, use a mechanical shaker.

7.2.4 Separate the sample from the mercury by drawing off the extract with a disposable pipet and transfer to a clean vial.

7.3 Removal of sulfur using TBA sulfite

7.3.1 Concentrate the sample extract to exactly 1.0 mL or other known volume. Perform concentration using the Kuderna-Danish (K-D) Technique (Method 3510, Sections 7.10.1 through 7.10.4).

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.3.2 Transfer 1.0 mL of the extract to a 50 mL clear glass bottle or vial with a Teflon-lined screw-cap. Rinse the concentrator tube with 1 mL of hexane, adding the rinsings to the 50 mL bottle.

7.3.3 Add 1.0 mL TBA sulfite reagent and 2 mL 2-propanol, cap the bottle, and shake for at least 1 min. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 0.100 g portions until a solid residue remains after repeated shaking.

7.3.4 Add 5 mL organic free reagent water and shake for at least 1 min. Allow the sample to stand for 5-10 min. Transfer the hexane layer (top) to a concentrator tube and concentrate the extract to approximately 1.0 mL with the micro K-D Technique (Section 7.3.5) or the Nitrogen Blowdown Technique (Section 7.3.6). Record the actual volume of the final extract.

7.3.5 Micro-Snyder Column Technique

7.3.5.1 Add another one or two clean boiling chips to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding about 0.5 mL of hexane to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively

chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints with about 0.2 mL of solvent and add to the concentrator tube. Adjust the final volume to approximately 1.0 mL with hexane.

7.3.6 Nitrogen Blowdown Technique

7.3.6.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to 1.0-2.0 mL, using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: Do not use plasticized tubing between the carbon trap and the sample.

7.3.6.2 The internal wall of the tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.4 Analyze the cleaned up extracts by gas chromatography (see the determinative methods, Section 4.3 of this chapter).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 All reagents should be checked prior to use to verify that interferences do not exist.

9.0 METHOD PERFORMANCE

9.1 Table 1 indicates the effect of using copper and mercury to remove sulfur on the recovery of certain pesticides.

10.0 REFERENCES

1. Loy, E.W., private communication.

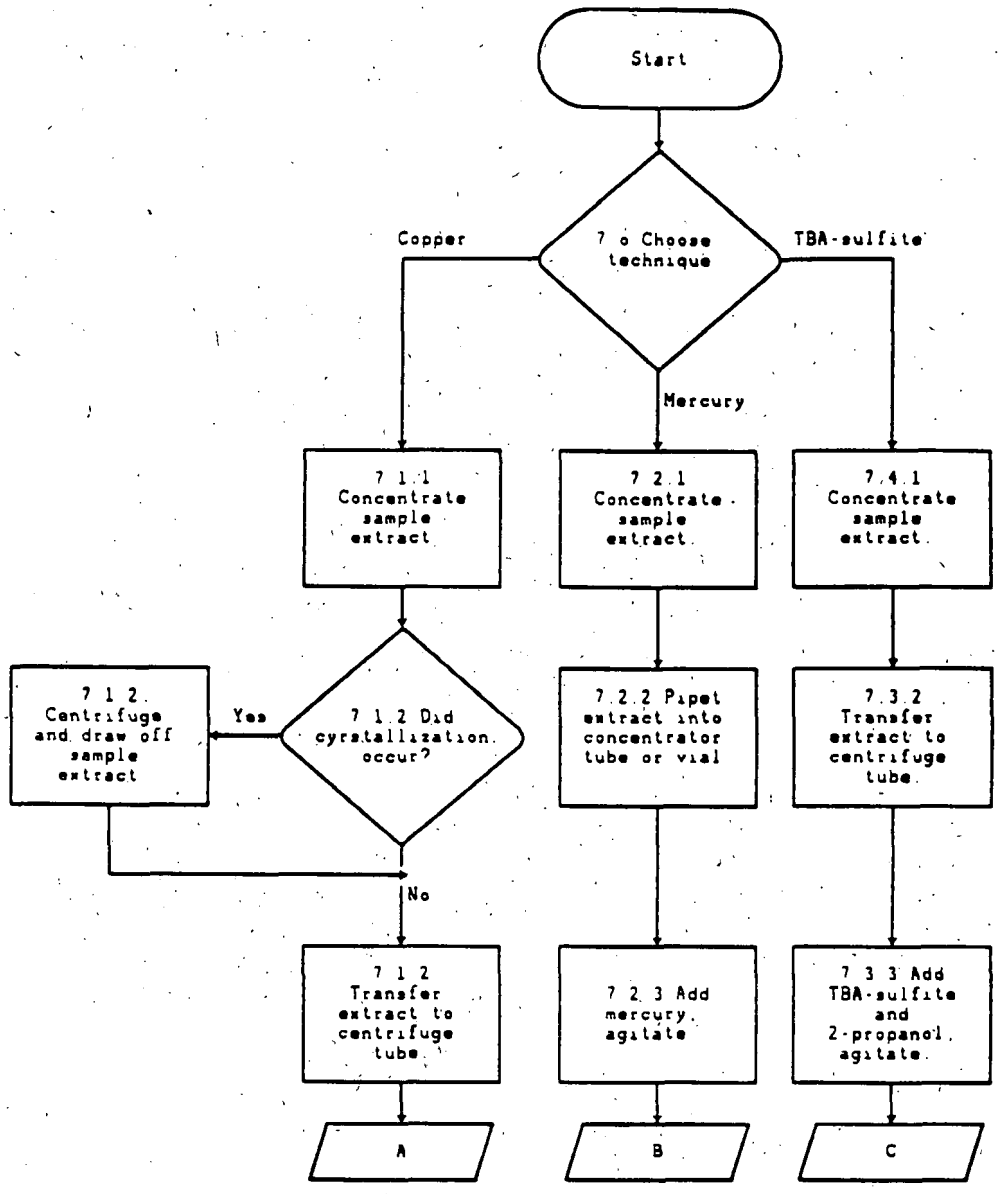
2. Goerlitz, D.F. and L.M. Law, Bulletin for Environmental Contamination and Toxicology, 6, 9 (1971).

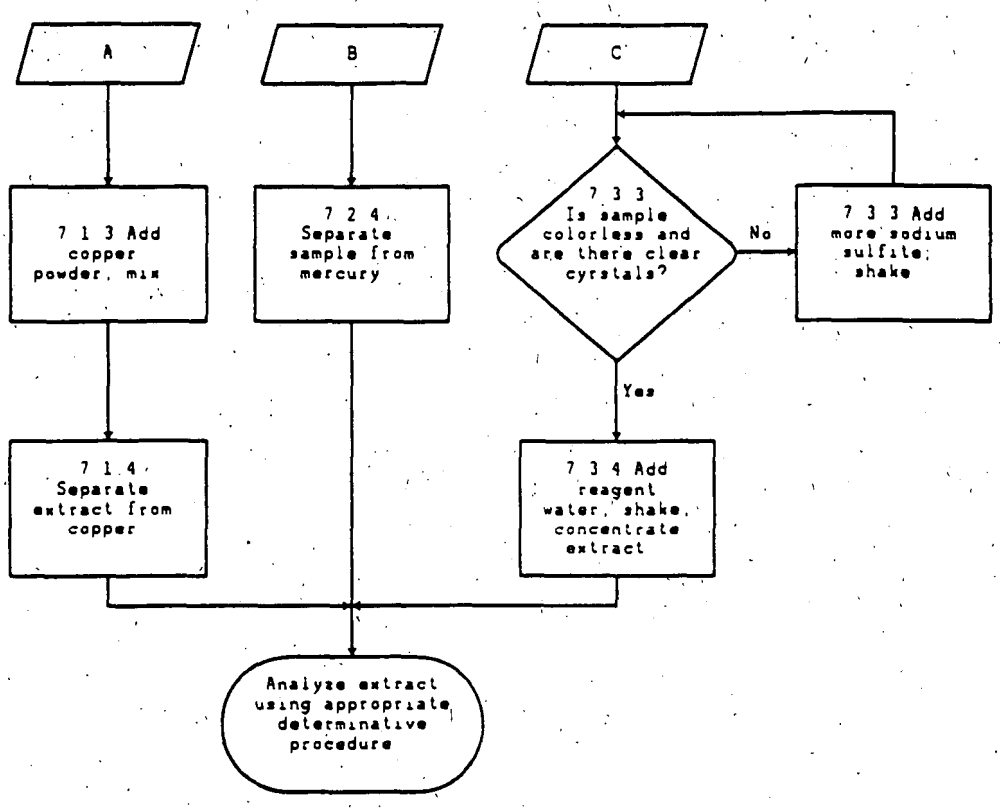
3. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, Revision, July 1985.

Table 1.
EFFECT OF MERCURY AND COPPER ON PESTICIDES

Pesticide	Percent Recovery[a] using: Mercury	Copper
Aroclor 1254	97.10	104.26
Lindane	75.73	94.83
Heptachlor	39.84	5.39
Aldrin	95.52	93.29
Heptachlor epoxide	69.13	96.55
DDE	92.07	102.91
DDT	78.78	85.10
BHC	81.22	98.08
Dieldrin	79.11	94.90
Endrin	70.83	89.26
Chlorobenzilate	7.14	0.00
Malathion	0.00	0.00
Diazinon	0.00	0.00
Parathion	0.00	0.00
Ethion	0.00	0.00
Trithion	0.00	0.00

a Percent recoveries cited are averages based on duplicate analyses for all compounds other than for Aldrin and BHC. For Aldrin, four and three determinations were averaged to obtain the result for mercury and copper, respectively. Recovery of BHC using copper is based on one analysis.


Start
7.0 Choose technique
Copper
Mercury
TBA-sulfite
7.1.1 Concentrate sample extract
7.2.1 Concentrate sample extract
7.4.1 Concentrate sample extract
7.1.2 Did cyrstallization occur?
Yes
7.1.2 Centrifuge and draw off sample extract
No
7.2.2 Pipet extract into concentrator tube or vial
7.3.2 Transfer extract to centrifuge tube
7.1.2 Transfer extract to centrifuge tube
7.2.3 Add mercury, agitate
7.3.3 Add TBA-sulfite and 2-propanol, agitate
A
B
C


A
B
C
7 1 3 Add copper powder, mix
7 2 4 Separate sample from mercury
7 3 3 Is sample colorless and are there clear cyrstals?
No
7 3 3 Add more sodium sulfite, shake
Yes
7 1 4 Separate extract from copper
7 3 4 Add reagent water, shake, concentrate extract
Analyze extract using appropriate determinative procedure

METHOD 3665

SULFURIC ACID/PERMANGANATE CLEANUP

1.0 SCOPE AND APPLICATION

1.1 This method is suitable for the rigorous cleanup of sample extracts prior to analysis for polychlorinated biphenyls. This method should be used whenever elevated baselines or overly complex chromatograms prevent accurate quantitation of PCBs. This method cannot be used to cleanup extracts for other target analytes, as it will destroy most organic chemicals including the pesticides Aldrin, Dieldrin, Endrin, Endosulfan (I and II), and Endosulfan sulfate.

2.0 SUMMARY OF METHOD

2.1 An extract is solvent exchanged to hexane, then the hexane is sequentially treated with (1) concentrated sulfuric acid and, if necessary, (2) 5% aqueous potassium permanganate. Appropriate caution must be taken with these corrosive reagents.

2.2 Blanks and replicate analysis samples must be subjected to the same cleanup as the samples associated with them.

2.3 It is important that all the extracts be exchanged to hexane before initiating the following treatments.

3.0 INTERFERENCES

3.1 This technique will not destroy chlorinated benzenes, chlorinated naphthalenes (Halowaxes), and a number of chlorinated pesticides.

4.0 APPARATUS

4.1 Syringe or Class A volumetric pipet, glass; 1.0, 2.0 and 5.0 mL.

4.2 Vials - 1, 2 and 10 mL, glass with Teflon lined screw caps or crimp tops.

4.3 Kuderna-Danish (K-D) apparatus.

4.3.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.4 Vortex mixer.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sulfuric acid/Water, H_2SO_4/H_2O, (1:1, v/v).

5.4 Hexane, C_6H_{14} - Pesticide grade or equivalent.

5.5 Potassium permanganate, $KMnO_4$, 5 percent aqueous solution (w/v).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Sulfuric acid cleanup

7.1.1 Using a syringe or a volumetric pipet, transfer 1.0 or 2.0 mL of the hexane extract to a 10 mL vial and, in a fume hood, carefully add 5 mL of the 1:1 sulfuric acid/water solution.

7.1.2 The volume of hexane extract used depends on the requirements of the GC autosampler used by the laboratory. If the autosampler functions reliably with 1 mL of sample volume, 1.0 mL of extract should be used. If the autosampler requires more than 1 mL of sample volume, 2.0 mL of extract should be used.

<u>CAUTION</u>: Make sure that there is no exothermic reaction nor evolution of gas prior to proceeding.

7.1.3 Cap the vial tightly and vortex for one minute. A vortex must be visible in the vial.

CAUTION: Stop the vortexing immediately if the vial leaks, AVOID SKIN CONTACT, SULFURIC ACID BURNS.

7.1.4 Allow the phases to separate for at least 1 minute. Examine the top (hexane) layer; it should not be highly colored nor should it have a visible emulsion or cloudiness.

7.1.5 If a clean phase separation is achieved, proceed to Sec. 7.1.8.

7.1.6 If the hexane layer is colored or the emulsion persists for several minutes, remove the sulfuric acid layer from the vial and dispose of it properly. Add another 5 mL of the clean 1:1 sulfuric acid/water.

NOTE: Do not remove any hexane at this stage of the procedure.

7.1.7 Vortex the sample for one minute and allow the phases to separate.

7.1.8 Transfer the hexane layer to a clean 10 mL vial.

7.1.9 Add an additional 1 mL of hexane to the sulfuric acid layer, cap and shake. This second extraction is done to ensure quantitative transfer of the PCBs and Toxaphene.

7.1.10 Remove the second hexane layer and combine with the hexane from Sec. 7.1.8.

7.2 Permanganate cleanup

7.2.1 Add 5 mL of the 5 percent aqueous potassium permanganate solution to the combined hexane fractions from 7.1.10.

CAUTION: Make sure that there is no exothermic reaction nor evolution of gas prior to proceeding.

7.2.2 Cap the vial tightly and vortex for 1 minute. A vortex must be visible in the vial.

CAUTION: Stop the vortexing immediately if the vial leaks. AVOID SKIN CONTACT, POTASSIUM PERMANGANATE BURNS.

7.2.3 Allow the phases to separate for at least 1 minute. Examine the top (hexane) layer, it should not be highly colored nor should it have a visible emulsion or cloudiness.

7.2.4 If a clean phase separation is achieved, proceed to Sec. 7.2.7.

7.2.5 If the hexane layer is colored or the emulsion persists for several minutes, remove the permanganate solution from the vial via a glass pipette and dispose of it properly. Add another 5 mL of the clean aqueous permanganate solution.

NOTE: Do not remove any hexane at this stage of the procedure.

7.2.6 Vortex the sample and allow the phases to separate.

7.2.7 Transfer the hexane layer to a clean 10 mL vial.

7.2.8 Add an additional 1 mL of hexane to the permanganate layer, cap the vial securely and shake. This second extraction is done to ensure quantitative transfer of the PCBs and Toxaphene.

7.2.9 Remove the second hexane layer and combine with the hexane from Sec. 7.2.7.

7.3 Final preparation

7.3.1 Reduce the volume of the combined hexane layers to the original volume (1 or 2 mL) using the Kuderna-Danish Technique (Sec. 7.3.1.1).

7.3.1.1 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of hexane to the top of the column. Place the K-D apparatus on a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.3.1.2 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of hexane. The extract may be further concentrated by using either the micro Snyder column technique (Sec. 7.3.2) or nitrogen blowdown technique (Sec. 7.3.3).

7.3.2 Micro Snyder Column Technique

7.3.2.1 Add another one or two clean boiling chips to the concentrator tube and attach a two ball micro Snyder column. Prewet the column by adding about 0.5 mL of hexane to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the

proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints with about 0.2 mL of hexane and add to the concentrator tube. Adjust the final volume to 1.0-2.0 mL, as required, with hexane.

7.3.3 Nitrogen Blowdown Technique

7.3.3.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: Do not use plasticized tubing between the carbon trap and the sample.

7.3.3.2 The internal wall of the tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

7.3.4 Remove any remaining organochlorine pesticides from the extracts using Florisil Column Cleanup (Method 3620) or Silica Gel Cleanup (Method 3630).

7.3.5 The extracts obtained may now be analyzed for the target analytes using the appropriate organic technique(s) (see Sec. 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store in a refrigerator. If the extract will be stored longer than 2 days, it should be transferred to a vial with a Teflon lined screw cap or crimp top, and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

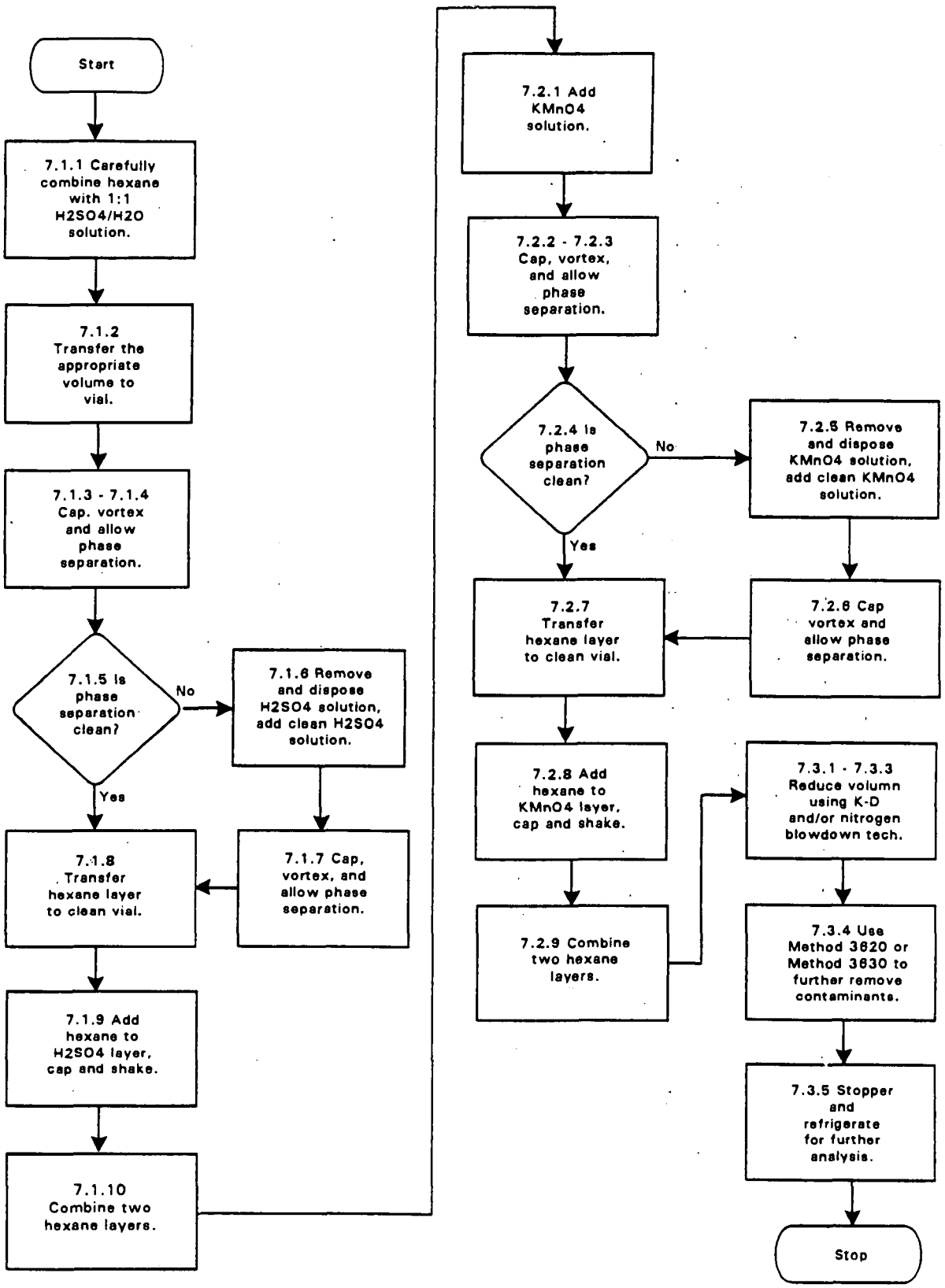
9.0 METHOD PERFORMANCE

9.1 No performance data are currently available.

10.0 REFERENCES

None required.

METHOD 3665
SULFURIC ACID/PERMANGANATE CLEANUP



METHOD 4010

SCREENING FOR PENTACHLOROPHENOL BY IMMUNOASSAY

1.0 SCOPE AND APPLICATION

1.1 Method 4010 is a procedure for screening solids such as soils, sludges, and aqueous media such as waste water and leachates for pentachlorophenol (PCP) (CAS Registry 87-86-5).

1.2 Method 4010 is recommended for screening samples to determine whether PCP is likely to be present at concentrations above 0.5 mg/Kg for solids or 0.005 mg/L for aqueous samples. Method 4010 provides an estimate for the concentration of PCP by comparison with a standard.

1.3 Using the test kits from which this method was developed, 95 % of aqueous samples containing 2 ppb or less of PCPs will produce a negative result in the 5 ppb test configuration. Also, 95 % of soil samples containing 125 ppb or less of PCBs will produce a negative result in the 500 ppb test configuration.

1.4 In cases where the exact concentration of PCP is required, additional techniques (i.e., gas chromatography (Method 8040) or gas chromatography/mass spectrometry (Method 8270)) should be used.

2.0 SUMMARY OF METHOD

2.1 Test kits are commercially available for this method. The manufacturer's directions should be followed. In general, the method is performed using a water sample or an extract of a soil sample. Sample and an enzyme conjugate reagent are added to immobilized antibody. The enzyme conjugate "competes" with PCP present in the sample for binding to immobilized anti-PCP antibody. The test is interpreted by comparing the response produced by testing a sample to the response produced by testing standard(s) simultaneously.

3.0 INTERFERENCES

3.1 Compounds that are chemically similar may cause a positive test (false positive) for PCP. The test kit used in preparation of this method was evaluated for interferences. Table 1 provides the concentration of compounds found to give a false positive test at the indicated concentration.

3.2 Other compounds have been tested for cross reactivity with PCP, and have been demonstrated to not interfere with the specific kit tested. Consult the information provided by the manufacturer of the kit used for additional information regarding cross reactivity with other compounds.

3.3 Storage and use temperatures may modify the method performance. Follow the manufacturer's directions for storage and use.

4.0 APPARATUS AND MATERIALS

4.1 PENTA RISc Test Kits (EnSys, Inc.), or equivalent. Each commercially available test kit will supply or specify the apparatus and materials necessary for successful completion of the test.

5.0 REAGENTS

5.1 Each commercially available test kit will supply or specify the reagents necessary for successful completion of the test.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Follow the manufacturer's instructions for the test kit being used. Those test kits used must meet or exceed the performance indicated in Tables 2-3.

8.0 QUALITY CONTROL

8.1 Follow the manufacturer's instructions for the test kit being used for quality control procedures specific to the test kit used. Additionally, guidance provided in Chapter One should be followed.

8.2 Use of replicate analyses, particularly when results indicate concentrations near the action level, is recommended to refine information gathered with the kit.

8.3 Do not use test kits past their expiration date.

8.4 Do not use tubes or reagents designated for use with other kits.

8.5 Use the test kits within their specified storage temperature and operating temperature limits.

8.6 Method 4010 is intended for field or laboratory use. The appropriate level of quality assurance should accompany the application of this method to document data quality.

9.0 METHOD PERFORMANCE

9.1 This method has been applied to a series of groundwater, process water, and wastewater samples from industries which use PCP, and the results compared with GC/MS determination of PCP (Method 8270). These results are provided in Table 2. These results represent determinations by two laboratories.

9.2 This method has been applied to a series of soils from industries which use PCP and the results compared with GC/MS determination of PCP via Method 8270. These results are provided in Table 3. These results represent determinations by two laboratories.

10.0 REFERENCES

1. J.P. Mapes, K.D. McKenzie, L.R. McClelland, S. Movassaghi, R.A. Reddy, R.L. Allen, and S.B. Friedman, "Rapid, On-Site Screening Test for Pentachlorophenol in Soil and Water - PENTA-RISc™", Ensys Inc., Research Triangle Park, NC 27709

2. J.P. Mapes, K.D. McKenzie, L.R. McClelland, S. Movassaghi, R.A. Reddy, R.L. Allen, and S.B. Friedman, "PENTA-RISc™ - An On-Site Immunoassay for Pentachlorophenol in Soil", Bull. Environ. Contam. Toxicol., 49:334-341, 1992.

3. PENTA-RISc™ Instructions for Use, Ensys Inc.

Table 1 Cross Reactivity for PCP[a]		
Compound	Concentration (mg/Kg) in Soil to Cause a False Positive for PCP at 0.5 mg/Kg	Concentration (μg/L) in Water to Cause a False Positive for PCP at 5 μg/L
2,6-Dichlorophenol	700	600
2,4,6-Trichlorophenol	16	100
2,4,5-Trichlorophenol	100	500
2,3,4-Trichlorophenol	400	600
2,3,5,6-Tetrachlorophenol	1.2	7
Tetrachlorohydroquinone	500	>1500

[a] for PENTA RISc Test Kit (EnSys, Inc.)

Table 2
Comparison of Immunoassay[a] with GC/MS
Water Matrix

Sample Type	Screening Results (ppm)							Concentration measured by GC/MS	Does screening test agree with GC/MS determination?
	0.005	0.05	0.1	0.5	1	5	50		
groundwater					>	>	<	3.5	no
			>	<				0.35	yes
	>	<						<0.1	yes
						>	<	8.2	yes
					>	<		2.8	yes
					>	<		2.9	yes
process water	>	>	<	<				0.21	no
	>	>	>	<				0.17	yes
			>	<				0.12	yes
wastewater		>	>	<	<			0.6	no
					>	<		1.4	yes
	>	>	<					<0.1	yes
			>	<				0.17	yes
run-off	>	>	<					<0.1	yes
	>	<						0.034	yes
		>			<			0.098	yes
		>			<			0.084	yes
		>			<			0.086	yes
						>		2.1	no
		>			<			0.073	yes
		>			<			0.026	no
	>	<						0.006	yes
					>			0.169	no
		>			<			0.239	yes
					>			0.190	no
					>			0.114	no
			>			<		0.346	yes
						>		1.1	yes
						>		19	yes
					>		<	4.3	yes

> = screening test indicates that the sample concentration is greater than the test concentration

< = screening test indicates that the sample concentration is less than the test concentration

[a] for PENTA RISc Test Kit (EnSys, Inc.)

Table 3
Comparison of Immunoassay[a] with GC/MS
Soil Matrix

Screening Results (ppm)			Concentration measured by GC/MS	Does screening test agree with GC/MS determination?
0.5	5	50		
>	>	>	1100	yes
>	>	<	88	no
<	<	<	0.31	yes
<	<	<	0.72	no
>	>	>	315	yes
>	<	<	1.5	yes
>	>	<	6.4	yes
>	>	<	9	yes
>	<	<	1.9	yes
>	>	>	46	no
>	<	<	<1	yes
>	>	<	21	yes
>	<	<	3.3	yes
>	>	<	4	no
>	>	<	11	yes
>	>	<	18	yes
>	>	<	33	yes
>	>	>	54	yes
>	>	>	65	yes
>	>	>	74	yes
>	>	>	83	yes
>	<	<	1.1	yes
>	>	<	14.3	yes
<	<	<	<1	yes
<	<	<	<1	yes
<	<	<	<1	yes
>	<	<	3.9	yes
<	<	<	<1	yes
>	<	<	1.4	yes
>	>	>	48	no
<	<	<	<1	yes
>	>	>	142	yes
>	>	<	108	no

Table 3 Continued				
Screening Results (ppm)			Concentration measured by GC/MS	Does screening test agree with GC/MS determination?
0.5	5	50		
>	>	>	117	yes
>	>	>	56	yes
>	<	<	2.5	yes
>	>	<	3.5	no
>	>	>	143	yes
<	<	<	nd	yes
<	<	<	0.02	yes
>	<	<	5	yes

> = screening test indicates that the sample concentration is greater than the test concentration

< = screening test indicates that the sample concentration is less than the test concentration

[a] for PENTA RISc Test Kit (EnSys, Inc.)

METHOD 5030A

PURGE-AND-TRAP

1.0 SCOPE AND APPLICATION

1.1 This method describes sample preparation and extraction for the analysis of volatile organics by a purge-and-trap procedure. The gas chromatographic determinative steps are found in Methods 8010, 8015, 8020, 8021 and 8030. Although applicable to Methods 8240 and 8260, the purge-and-trap procedure is already incorporated into Methods 8240 and 8260.

1.2 Method 5030 can be used for most volatile organic compounds that have boiling points below 200°C and are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax or a coated capillary column. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.

1.3 Water samples can be analyzed directly for volatile organic compounds by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in water can be determined by direct injection of the sample into the chromatographic system.

1.4 This method also describes the preparation of water-miscible liquids, non-water-miscible liquids, solids, wastes, and soils/sediments for analysis by the purge-and-trap procedure.

2.0 SUMMARY OF METHOD

2.1 The purge-and-trap process: An inert gas is bubbled through the solution at ambient temperature, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column.

2.2 If the sample introduction technique in Section 2.1 is not applicable, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is combined with water in a specially designed purging chamber. It is then analyzed by purge-and-trap GC following the normal water method.

3.0 INTERFERENCES

3.1 Impurities in the purge gas, and from organic compounds out-gassing from the plumbing ahead of the trap, account for the majority of contamination problems. The analytical system must be demonstrated to be free from

contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE plastic coating, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by an analysis of organic-free reagent water to check for cross-contamination. The trap and other parts of the system are subject to contamination. Therefore, frequent bake-out and purging of the entire system may be required.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringes - 10 µL, 25 µL, 100 µL, 250 µL, 500 µL, and 1,000 µL. These syringes should be equipped with a 20 gauge (0.006 in ID) needle having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device. The needle length will depend upon the dimensions of the purging device employed.

4.2 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.3 Syringe - 5 mL, gas-tight with shutoff valve.

4.4 Analytical balance - 0.0001 g.

4.5 Top-loading balance - 0.1 g.

4.6 Glass scintillation vials - 20 mL, with screw-caps and Teflon liners or glass culture tubes with screw-caps and Teflon liners.

4.7 Volumetric flasks, Class A - 10 mL and 100 mL, with ground-glass stoppers.

4.8 Vials - 2 mL, for GC autosampler.

4.9 Spatula - Stainless steel.

4.10 Disposable pipets - Pasteur.

4.11 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

4.11.1 The recommended purging chamber is designed to accept 5 mL samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1, meets these design criteria. Alternate sample purge devices may be used, provided equivalent performance is demonstrated.

4.11.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap must contain the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap (see Figures 2 and 3). If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

4.11.3 The desorber should be capable of rapidly heating the trap to 180°C for desorption. The polymer section of the trap should not be heated higher than 180°C, and the remaining sections should not exceed 220°C during bake-out mode. The desorber design illustrated in Figures 2 and 3 meet these criteria.

4.11.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 4 and 5.

4.11.5 Trap Packing Materials

4.11.5.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.11.5.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.11.5.3 Silica gel - 35/60 mesh, Davison, grade 15 or equivalent.

4.11.5.4 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26 lot #M-2649, or equivalent, by crushing through 26 mesh screen.

4.12 Heater or heated oil bath - capable of maintaining the purging chamber to within 1°C, over a temperature range from ambient to 100°C.

5.0 REAGENTS

5.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Methanol, CH_3OH - Pesticide quality or equivalent. Store away from other solvents.

5.3 Reagent Tetraglyme - Reagent tetraglyme is defined as tetraglyme in which interference is not observed at the method detection limit of the compounds of interest.

5.3.1 Tetraglyme (tetraethylene glycol dimethyl ether, Aldrich #17, 240-5 or equivalent), $C_8H_{18}O_5$. Purify by treatment at reduced pressure in a rotary evaporator. The tetraglyme should have a peroxide content of less than 5 ppm as indicated by EM Quant Test Strips (available from Scientific Products Co., Catalog No. P1126-8 or equivalent).

CAUTION: Glycol ethers are suspected carcinogens. All solvent handling should be done in a hood while using proper protective equipment to minimize exposure to liquid and vapor.

Peroxides may be removed by passing the tetraglyme through a column of activated alumina. The tetraglyme is placed in a round bottom flask equipped with a standard taper joint, and the flask is affixed to a rotary evaporator. The flask is immersed in a water bath at 90-100°C and a vacuum is maintained at < 10 mm Hg for at least two hours using a two stage mechanical pump. The vacuum system is equipped with an all glass trap, which is maintained in a dry ice/methanol bath. Cool the tetraglyme to ambient temperature and add 100 mg/L of 2,6-di-tert-butyl-4-methyl-phenol to prevent peroxide formation. Store the tetraglyme in a tightly sealed screw cap bottle in an area that is not contaminated by solvent vapors.

5.3.2 In order to demonstrate that all interfering volatiles have been removed from the tetraglyme, an organic-free reagent water/tetraglyme blank must be analyzed.

5.4 Polyethylene glycol, $H(OCH_2CH_2)_nOH$. Free of interferences at the detection limit of the analytes.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to the introductory material to this chapter, Organic Analytes, Section 4.1. Samples should be stored in capped bottles, with minimum headspace, at 4°C or less.

7.0 PROCEDURE

7.1 Initial calibration: Prior to using this introduction technique for any GC method, the system must be calibrated. General calibration procedures are discussed in Method 8000, while the specific determinative methods and Method 3500 give details on preparation of standards.

7.1.1 Assemble a purge-and-trap device that meets the specification in Section 4.10. Condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 mL/min. Prior to use, condition the trap daily for 10 min while backflushing at 180°C with the column at 220°C.

7.1.2 Connect the purge-and-trap device to a gas chromatograph.

7.1.3 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device. Add 5.0 mL of organic-free reagent water to the purging device. The organic-free reagent water is added to the purging device using a 5 mL glass syringe fitted with a 15 cm 20-gauge needle. The needle is inserted through the sample inlet shown in Figure 1. The internal diameter of the 14-gauge needle that forms the sample inlet will permit insertion of the 20-gauge needle. Next, using a 10 µL or 25 µL micro-syringe equipped with a long needle (Section 4.1), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards. Add the aliquot of calibration solution directly to the organic-free reagent water in the purging device by inserting the needle through the sample inlet. When discharging the contents of the micro-syringe, be sure that the end of the syringe needle is well beneath the surface of the organic-free reagent water. Similarly, add 10 µL of the internal standard solution. Close the 2-way syringe valve at the sample inlet.

7.1.4 Carry out the purge-and-trap analysis procedure using the specific conditions given in Table 1.

7.1.5 Calculate response factors or calibration factors for each analyte of interest using the procedure described in Method 8000.

7.1.6 The average RF must be calculated for each compound. A system performance check should be made before this calibration curve is used. If the purge-and-trap procedure is used with Method 8010, the following five compounds are checked for a minimum average response factor: chloromethane; 1,1-dichloroethane; bromoform; 1,1,2,2-tetrachloroethane; and chlorobenzene. The minimum acceptable average RF for these compounds should be 0.300 (0.250 for bromoform). These compounds typically have RFs of 0.4-0.6, and are used to check compound stability and to check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

7.1.6.1 Chloromethane: This compound is the most likely compound to be lost if the purge flow is too fast.

7.1.6.2 Bromoform: This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow.

Cold spots and/or active sites in the transfer lines may adversely affect response.

7.1.6.3 Tetrachloroethane and 1,1-dichloroethane: These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2 On-going calibration: Refer to Method 8000 for details on continuing calibration.

7.3 Sample preparation

7.3.1 Water samples

7.3.1.1 Screening of the sample prior to purge-and-trap analysis will provide guidance on whether sample dilution is necessary and will prevent contamination of the purge-and-trap system. Two screening techniques that can be utilized are: the use of an automated headspace sampler (modified Method 3810), interfaced to a gas chromatograph (GC), equipped with a photo ionization detector (PID), in series with an electrolytic conductivity detector (HECD); and extraction of the sample with hexadecane (Method 3820) and analysis of the extract on a GC with a FID and/or an ECD.

7.3.1.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.3.1.3 Assemble the purge-and-trap device. The operating conditions for the GC are given in Section 7.0 of the specific determinative method to be employed.

7.3.1.4 Daily GC calibration criteria must be met (Method 8000) before analyzing samples.

7.3.1.5 Adjust the purge gas flow rate (nitrogen or helium) to that shown in Table 1, on the purge-and-trap device. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response.

7.3.1.6 Remove the plunger from a 5 mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20 mL syringe would allow the use of only one

syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hr. Care must be taken to prevent air from leaking into the syringe.

7.3.1.7 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe.

7.3.1.7.1 Dilutions may be made in volumetric flasks (10 mL to 100 mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.3.1.7.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask selected and add slightly less than this quantity of organic-free reagent water to the flask.

7.3.1.7.3 Inject the proper aliquot of samples from the syringe prepared in Section 7.3.1.5 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat the above procedure for additional dilutions.

7.3.1.7.4 Fill a 5 mL syringe with the diluted sample as in Section 7.3.1.5.

7.3.1.8 Add 10.0 µL of surrogate spiking solution (found in each determinative method, Section 5.0) and, if applicable, 10 µL of internal standard spiking solution through the valve bore of the syringe; then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. Matrix spiking solutions, if indicated, should be added (10 µL) to the sample at this time.

7.3.1.9 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

7.3.1.10 Close both valves and purge the sample for the time and at the temperature specified in Table 1.

7.3.1.11 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program and GC data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C while backflushing the trap with inert gas between 20 and 60 mL/min for the time specified in Table 1.

7.3.1.12 While the trap is being desorbed into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of organic-free reagent water (or

methanol followed by organic-free reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

7.3.1.13 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 sec; then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C for Methods 8010, 8020, 8021, 8240 and 8260 and 210°C for Methods 8015 and 8030. Trap temperatures up to 220°C may be employed. However, the higher temperatures will shorten the useful life of the trap. After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

7.3.1.14 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample is analyzed that has saturated response from a compound, this analysis must be followed by a blank organic-free reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

7.3.1.15 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Proceed to Method 8000 and the specific determinative method for details on calculating analyte response.

7.3.2 Water-miscible liquids:

7.3.2.1 Water-miscible liquids are analyzed as water samples after first diluting them at least 50-fold with organic-free reagent water.

7.3.2.2 Initial and serial dilutions can be prepared by pipetting 2 mL of the sample into a 100 mL volumetric flask and diluting to volume with organic-free reagent water. Transfer immediately to a 5 mL gas-tight syringe.

7.3.2.3 Alternatively, prepare dilutions directly in a 5 mL syringe filled with organic-free reagent water by adding at least 20 µL, but not more than 100 µL of liquid sample. The sample is ready for addition of surrogate and, if applicable, internal and matrix spiking standards.

7.3.3 Sediment/soil and waste samples: It is highly recommended that all samples of this type be screened prior to the purge-and-trap GC analysis. These samples may contain percent quantities of purgeable organics that will contaminate the purge-and-trap system, and require extensive cleanup and instrument downtime. See Section 7.3.1.1 for recommended screening techniques. Use the screening data to determine whether to use the low-concentration method (0.005-1 mg/kg) or the high-

concentration method (>1 mg/kg).

7.3.3.1 Low-concentration method: This is designed for samples containing individual purgeable compounds of <1 mg/kg. It is limited to sediment/soil samples and waste that is of a similar consistency (granular and porous). The low-concentration method is based on purging a heated sediment/soil sample mixed with organic-free reagent water containing the surrogate and, if applicable, internal and matrix spiking standards. Analyze all reagent blanks and standards under the same conditions as the samples.

7.3.3.1.1 Use a 5 g sample if the expected concentration is <0.1 mg/kg or a 1 g sample for expected concentrations between 0.1 and 1 mg/kg.

7.3.3.1.2 The GC system should be set up as in Section 7.0 of the specific determinative method. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and samples. A heated purge calibration curve must be prepared and used for the quantitation of all samples analyzed with the low-concentration method. Follow the initial and daily calibration instructions, except for the addition of a 40°C purge temperature for Methods 8010, 8020, and 8021.

7.3.3.1.3 Remove the plunger from a 5 mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with organic-free reagent water. Replace the plunger and compress the reagent water to vent trapped air. Adjust the volume to 5.0 mL. Add 10 µL each of surrogate spiking solution and internal standard solution to the syringe through the valve. (Surrogate spiking solution and internal standard solution may be mixed together.) Matrix spiking solutions, if indicated, should be added (10 µL) to the sample at this time.

7.3.3.1.4 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount determined in Section 7.3.3.1.1 into a tared purge device. Note and record the actual weight to the nearest 0.1 g.

7.3.3.1.5 Determination of sample % dry weight - In certain cases, sample results are desired based on dry weight basis. When such data is desired, a portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

<u>WARNING</u>: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily

contaminated hazardous waste sample.

7.3.3.1.5.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.3.3.1.6 Add the spiked organic-free reagent water to the purge device, which contains the weighed amount of sample, and connect the device to the purge-and-trap system.

NOTE: Prior to the attachment of the purge device, Sections 7.3.3.1.4 and 7.3.3.1.6 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

7.3.3.1.7 Heat the sample to 40°C ± 1°C (Methods 8010, 8020 and 8021) or to 85°C ± 2°C (Methods 8015 and 8030) and purge the sample for the time shown in Table 1.

7.3.3.1.8 Proceed with the analysis as outlined in Sections 7.3.1.11-7.3.1.15. Use 5 mL of the same organic-free reagent water as in the reagent blank. If saturated peaks occurred or would occur if a 1 g sample were analyzed, the high-concentration method must be followed.

7.3.3.1.9 For matrix spike analysis of low-concentration sediment/soils, add 10 µL of the matrix spike solution to 5 mL of organic-free reagent water (Section 7.3.3.1.3). The concentration for a 5 g sample would be equivalent to 50 µg/kg of each matrix spike standard.

7.3.3.2 High-concentration method: The method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol. Wastes (i.e. petroleum and coke wastes) that are insoluble in methanol are diluted with reagent tetraglyme or polyethylene glycol (PEG). An aliquot of the extract is added to organic-free reagent water containing surrogate and, if applicable, internal and matrix spiking standards. This is purged at the temperatures indicated in Table 1. All samples with an expected concentration of >1.0 mg/kg should be analyzed by this method.

7.3.3.2.1 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. For sediment/soil and waste that are insoluble in methanol, weigh

4 g (wet weight) of sample into a tared 20 mL vial. Use a top-loading balance. Note and record the actual weight to 0.1 gram and determine the percent dry weight of the sample using the procedure in Section 7.3.3.1.5. For waste that is soluble in methanol, tetraglyme, or PEG, weigh 1 g (wet weight) into a tared scintillation vial or culture tube or a 10 mL volumetric flask. (If a vial or tube is used, it must be calibrated prior to use. Pipet 10.0 mL of methanol into the vial and mark the bottom of the meniscus. Discard this solvent.)

7.3.3.2.2 For sediment/soil or solid waste, quickly add 9.0 mL of appropriate solvent; then add 1.0 mL of the surrogate spiking solution to the vial. For a solvent miscible sample, dilute the sample to 10 mL with the appropriate solvent after adding 1.0 mL of the surrogate spiking solution. Cap and shake for 2 min.

NOTE: Sections 7.3.3.2.1 and 7.3.3.2.2 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

7.3.3.2.3 Pipet approximately 1 mL of the extract into a GC vial for storage, using a disposable pipet. The remainder may be discarded. Transfer approximately 1 mL of reagent methanol to a separate GC vial for use as the method blank for each set of samples. These extracts may be stored at 4°C in the dark, prior to analysis.

7.3.3.2.4 The GC system should be set up as in Section 7.0 of the specific determinative method. This should be done prior to the addition of the methanol extract to organic-free reagent water.

7.3.3.2.5 Table 2 can be used to determine the volume of methanol extract to add to the 5 mL of organic-free reagent water for analysis. If a screening procedure was followed, use the estimated concentration to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low-concentration analysis to determine the appropriate volume. If the sample was submitted as a high-concentration sample, start with 100 µL. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.3.3.2.6 Remove the plunger from a 5.0 mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with organic-free reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of the sample extract and of

standards. Add 10 µL of internal standard solution. Also add the volume of methanol extract determined in Section 7.3.3.2.5 and a volume of methanol solvent to total 100 µL (excluding methanol in standards).

7.3.3.2.7 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the water/methanol sample into the purging chamber.

7.3.3.2.8 Proceed with the analysis as outlined in the specific determinative method. Analyze all reagent blanks on the same instrument as that used for the samples. The standards and blanks should also contain 100 µL of methanol to simulate the sample conditions.

7.3.3.2.9 For a matrix spike in the high-concentration sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spike solution and 1.0 mL of matrix spike solution. Add a 100 µL aliquot of this extract to 5 mL of water for purging (as per Section 7.3.3.2.6).

7.4 Sample analysis:

7.4.1 The samples prepared by this method may be analyzed by Methods 8010, 8015, 8020, 8021, 8030, 8240, and 8260. Refer to these methods for appropriate analysis conditions.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3500 for sample preparation procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of a calibration blank that all glassware and reagents are interference free. Each time a set of samples is extracted, or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of the sample preparation and measurement.

8.3 Standard quality assurance practices should be used with this method. Field duplicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Spiked samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the spiked samples do not indicate sufficient sensitivity to detect < 1 µg/g of the analytes in the sample, then the sensitivity of the instrument should be increased, or the sample should be subjected to additional cleanup.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

TABLE 1
PURGE-AND-TRAP OPERATING PARAMETERS

	Analysis Method			
	8010	8015	8020/8021	8030
Purge gas	Nitrogen or Helium	Nitrogen or Helium	Nitrogen or Helium	Nitrogen or Helium
Purge gas flow rate (mL/min)	40	20	40	20
Purge time (min)	11.0 ± 0.1	15.0 ± 0.1	11.0 ± 0.1	15.0 ± 0.1
Purge temperature (°C)	Ambient	85 ± 2	Ambient	85 ± 2
Desorb temperature (°C)	180	180	180	180
Backflush inert gas flow (mL/min)	20-60	20-60	20-60	20-60
Desorb time (min)	4	1.5	4	1.5

TABLE 2
QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH-CONCENTRATION SOILS/SEDIMENTS

Approximate Concentration Range	Volume of Methanol Extract[a]
500-10,000 µg/kg	100 µL
1,000-20,000 µg/kg	50 µL
5,000-100,000 µg/kg	10 µL
25,000-500,000 µg/kg	100 µL of 1/50 dilution [b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a]The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5 mL syringe whatever volume of methanol is necessary to maintain a volume of 100 µL added to the syringe.

[b]Dilute an aliquot of the methanol extract and then take 100 µL for analysis.

Figure 1
Purging Chamber

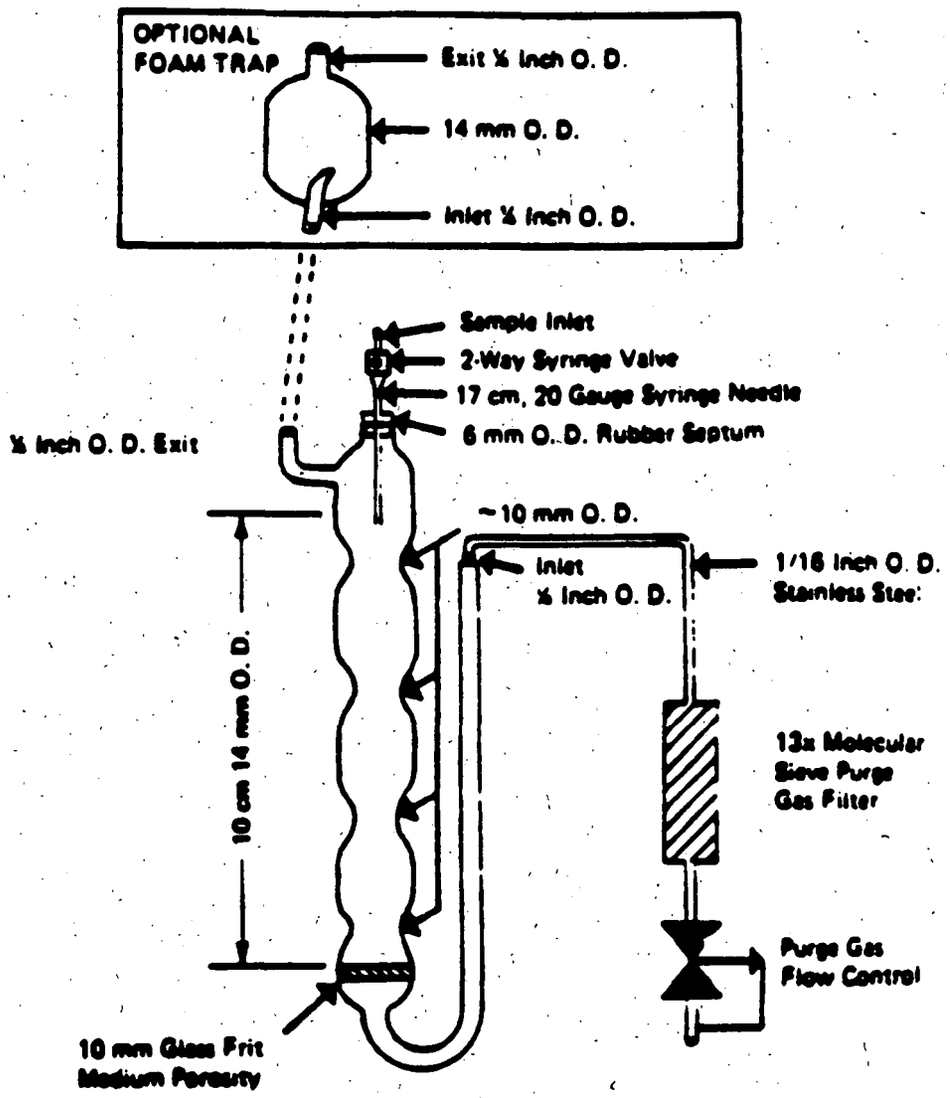


Figure 2
Trap Packing and Construction for Method 8010

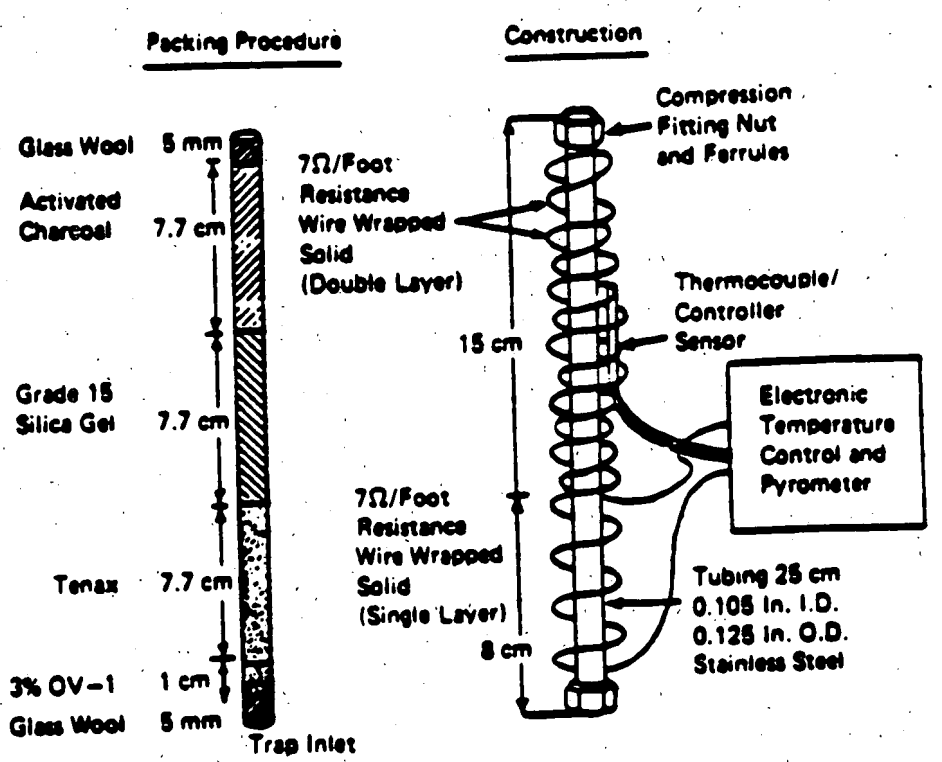


Figure 3
Trap Packing and Construction for Methods 8020 and 8030

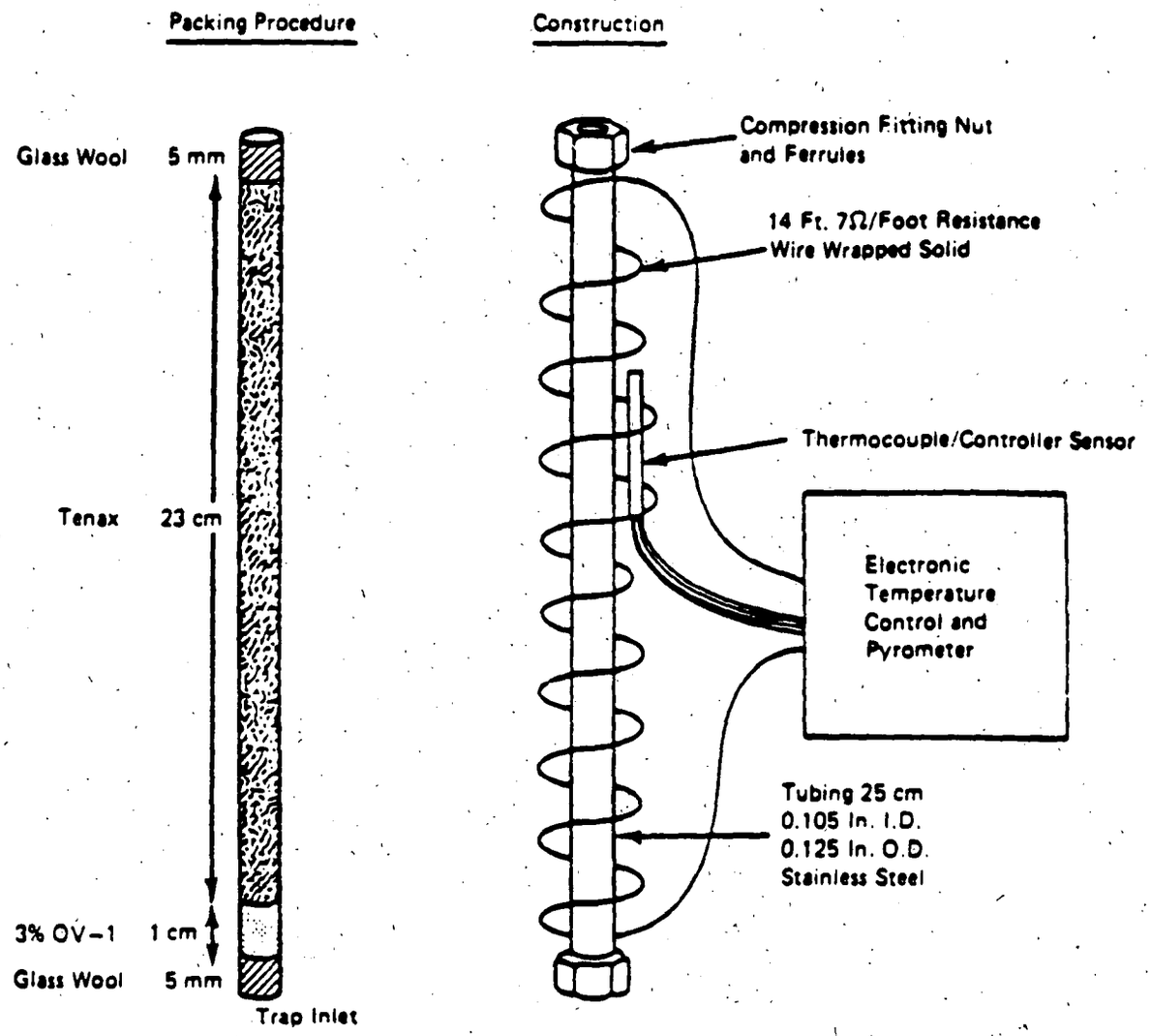


Figure 4
Purge-and-Trap System
Purge-Sorb Mode
For Method 8010, 8020, and 8030

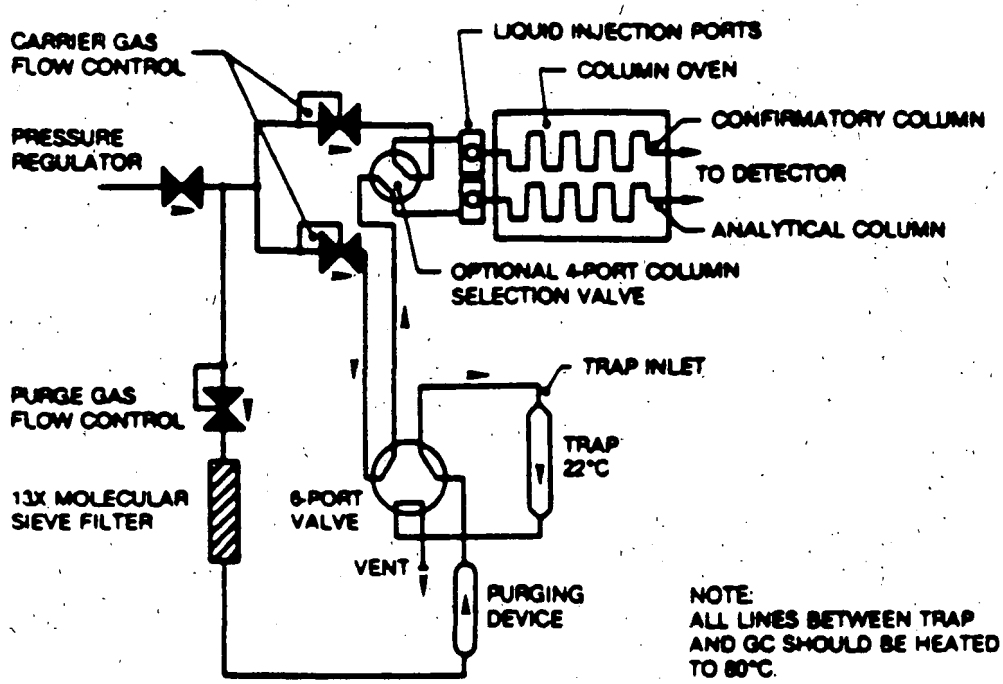
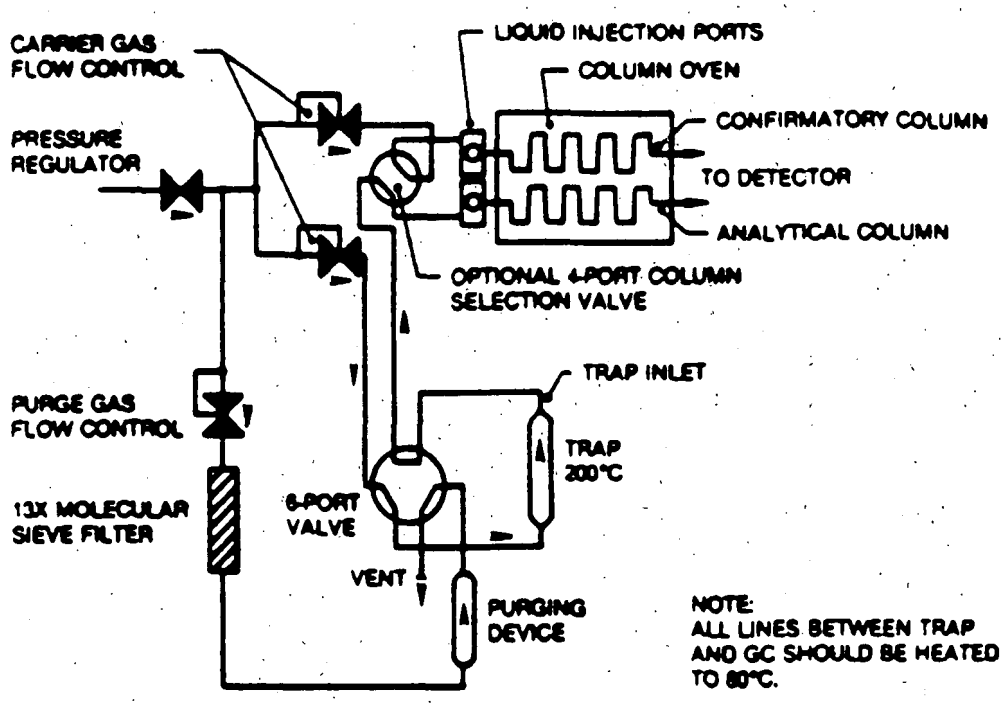
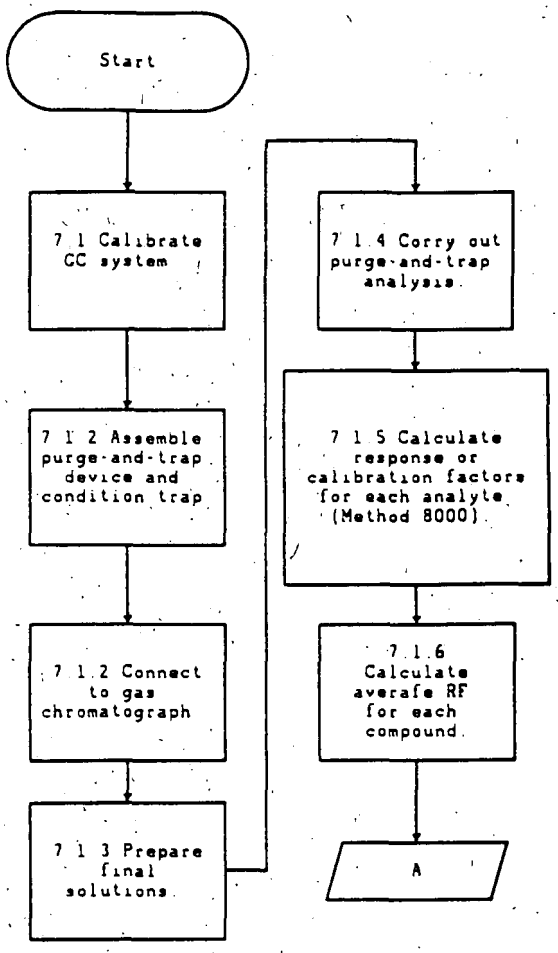
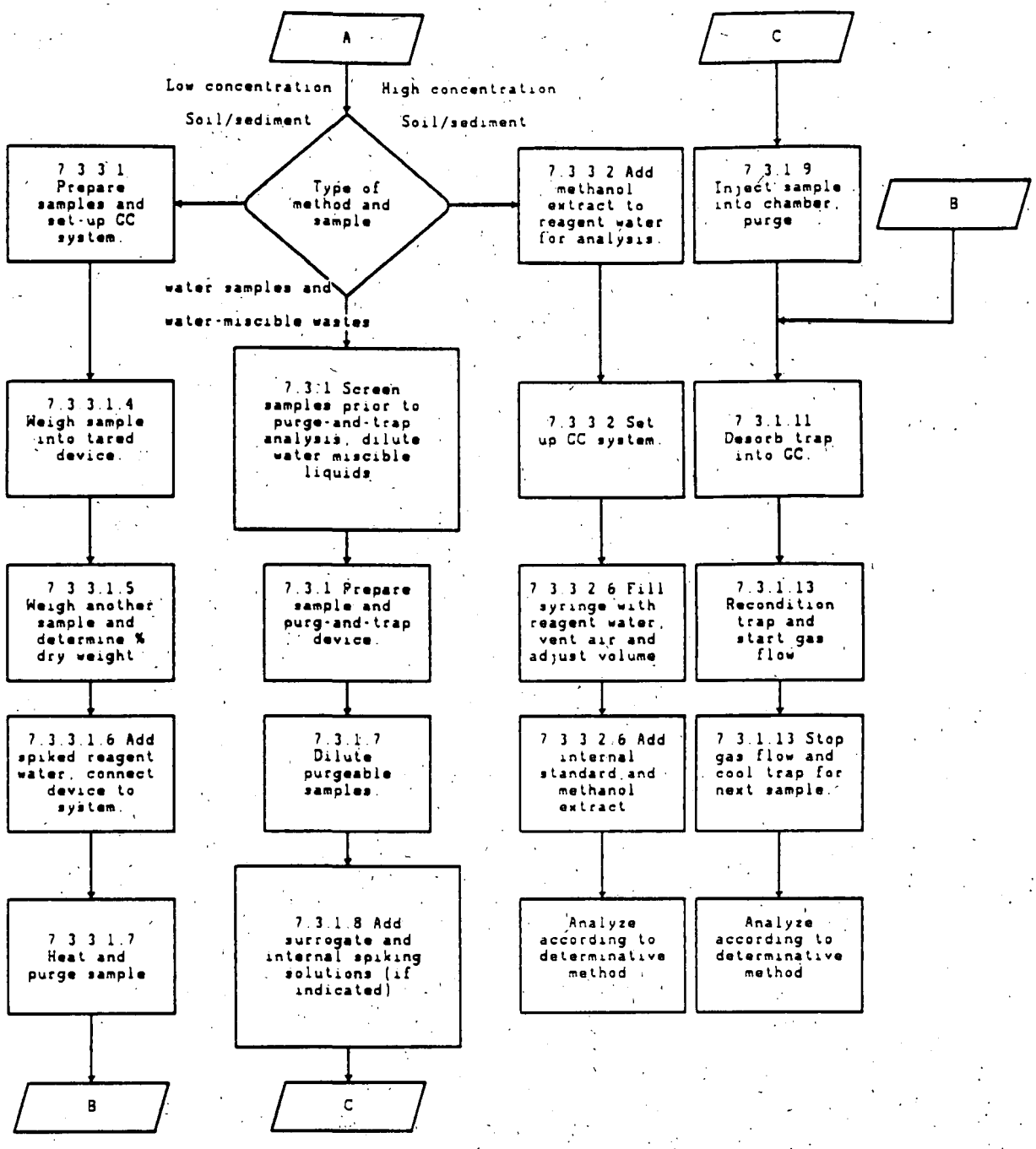


Figure 5
Purge-and-Trap System
Desorb Mode
For Method 8010, 8020, and 8030




Start
7.1 Calibrate GC system
7.1.2 Assemble purge-and-trap device and condition trap
7.1.2 Connect to gas chromatograph
7.1.3 Prepare final solutions
7.1.4 Carry out purge-and-trap analysis
7.1.5 Calculate response or calibration factors for each analyte (Method 8000)
7.1.6 Calculate average RF for each compound
A


A
C
Low concentration
Soil/sediment
High concentration
Soil/sediment
Type of method and sample
7.3.3.1 Prepare samples and set-up GC system.
7.3.3.2 Add methanol extract to reagent water for analysis.
7.3.1.9 Inject sample into chamber, purge
B
water samples and
water-miscible wastes
7.3.3.1.4 Weigh sample into tared device.
7.3.1 Screen samples prior to purge-and-trap analysis, dilute water miscible liquids
7.3.3.2 Set up GC system.
7.3.1.11 Desorb trap into GC.
7.3.3.1.5 Weigh another sample and determine % dry weight
7.3.1 Prepare sample and purg-and-trap device.
7.3.3.2.6 Fill syringe with reagent water, vent air and adjust volume
7.3.1.13 Recondition trap and start gas flow
7.3.3.1.6 Add spiked reagent water, connect device to system.
7.3.1.7 Dilute purgeable samples.
7.3.3.2.6 Add internal standard and methanol extract
7.3.1.13 Stop gas flow and cool trap for next sample.
7.3.3.1.7 Heat and purge sample
7.3.1.8 Add surrogate and internal spiking solutions (if indicated)
Analyze according to determinative method
Analyze according to determinative method
B
C

METHOD 5040A

ANALYSIS OF SORBENT CARTRIDGES FROM VOLATILE ORGANIC SAMPLING TRAIN (VOST): GAS CHROMATOGRAPHY/MASS SPECTROMETRY TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 5040 was formerly Method 3720 in the Second Edition of this manual.

1.2 This method covers the determination of volatile principal organic hazardous constituents (POHCs), collected on Tenax and Tenax/charcoal sorbent cartridges using a volatile organic sampling train, VOST (1). Much of the description for purge-and-trap GC/MS analysis is described in Method 8240 of this chapter. Because the majority of gas streams sampled using VOST will contain a high concentration of water, the analytical method is based on the quantitative thermal desorption of volatile POHCs from the Tenax and Tenax/charcoal traps and analysis by purge-and-trap GC/MS. For the purposes of definition, volatile POHCs are those POHCs with boiling points less than 100°C.

1.3 This method is applicable to the analysis of Tenax and Tenax/charcoal cartridges used to collect volatile POHCs from wet stack gas effluents from hazardous waste incinerators.

1.4 The sensitivity of the analytical method for a particular volatile POHC depends on the level of interferences and the presence of detectable levels of volatile POHCs in blanks. The desired target detection limit of the analytical method is 0.1 ng/L (20 ng on a single pair of traps) for a particular volatile POHC desorbed from either a single pair of Tenax and Tenax/charcoal cartridges or by thermal desorption of up to six pairs of traps onto a single pair of Tenax and Tenax/charcoal traps. The resulting single pair of traps is then thermally desorbed and analyzed by purge-and-trap GC/MS.

1.5 This method is recommended for use only by experienced mass spectroscopists or under the close supervision of such qualified persons.

2.0 SUMMARY OF METHOD

2.1 A schematic diagram of the analytical system is shown in Figure 1. The contents of the sorbent cartridges are spiked with an internal standard and thermally desorbed for 10 min at 180°C with organic-free nitrogen or helium gas (at a flow rate of 40 mL/min), bubbled through 5 mL of organic-free reagent water, and trapped on an analytical adsorbent trap. After the 10 min. desorption, the analytical adsorbent trap is rapidly heated to 180°C, with the carrier gas flow reversed so that the effluent flow from the analytical trap is directed into the GC/MS. The volatile POHCs are separated by temperature programmed gas chromatography and detected by low-resolution mass spectrometry. The concentrations of volatile POHCs are calculated using the internal standard technique.

3.0 INTERFERENCES

3.1 Refer to Methods 3500 and 8240.

4.0 APPARATUS AND MATERIALS

4.1 Thermal desorption unit:

4.1.1 The thermal desorption unit (for Inside/Inside VOST cartridges, use Supelco "clamshell" heater; for Inside/Outside VOST cartridges, user-fabricated unit is required) should be capable of thermally desorbing the sorbent resin tubes. It should also be capable of heating the tubes to 180 $\pm$ 10°C with flow of organic-free nitrogen or helium through the tubes.

4.2 Purge-and-trap unit:

4.2.1 The purge-and-trap unit consists of three separate pieces of equipment: the sample purger, trap, and the desorber. It should be capable of meeting all requirements of Method 5030 for analysis of purgeable organic compounds from water.

4.3 GC/MS system: As described in Method 8240.

5.0 REAGENTS

5.1 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Methanol, CH_3OH - Pesticide grade, or equivalent.

5.3 Analytical trap reagents:

5.3.1 2,6-Diphenylene oxide polymer: Tenax (60/80 mesh), chromatographic grade or equivalent.

5.3.2 Methyl silicone packing: 3% OV-1 on Chromosorb W (60/80 mesh) or equivalent.

5.3.3 Silica gel: Davison Chemical (35/00 mesh), Grade 15, or equivalent.

5.3.4 Charcoal: Petroleum-based (SKC Lot 104 or equivalent).

5.4 Stock standard solution:

5.4.1 Stock standard solutions will be prepared from pure standard materials or purchased as certified solutions. The stock standards should be prepared in methanol using assayed liquids or gases, as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA approved toxic

gas respirator should be used when the analyst handles high concentrations of such materials.

5.4.2 Fresh stock standards should be prepared weekly for volatile POHCs with boiling points of <35°C. All other standards must be replaced monthly, or sooner if comparison with check standards indicates a problem.

5.5 Secondary dilution standards:

5.5.1 Using stock standard solutions, prepare, in methanol, secondary dilution standards that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the desorbed calibration standards will bracket the working range of the analytical system.

5.6 4-Bromofluorobenzene (BFB) standard:

5.6.1 Prepare a 25 ng/μL solution of BFB in methanol.

5.7 Deuterated benzene:

5.7.1 Prepare a 25 ng/μL solution of benzene-d_6 in methanol.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to Method 0030, Chapter Ten.

6.2 Sample trains obtained from the VOST should be analyzed within 2-6 weeks of sample collection.

7.0 PROCEDURE

7.1 Assembly of PTD device:

7.1.1 Assemble a purge-and-trap desorption device (PTD) that meets all the requirements of Method 5030 (refer to Figure 1).

7.1.2 Connect the thermal desorption device to the PTD device. Calibrate the PTD-GC/MS system using the internal standard technique.

7.2 Internal standard calibration procedure:

7.2.1 This approach requires the use of deuterated benzene as the internal standard for these analyses. Other internal standards may be proposed for use in certain situations. The important criteria for choosing a particular compound as an internal standard are that it be similar in analytical behavior to the compounds of interest and that it can be demonstrated that the measurement of the internal standard be unaffected by method or matrix interferences. Other internal standards that have been used are ethylbenzene-d_{10} and, 1-2-dichloroethane-d_4. One adds 50 ng of BFB to all sorbent cartridges (in addition to one or more

internal standards) to provide continuous monitoring of the GC/MS performance relative to BFB.

7.2.2 Prepare calibration standards at a minimum of three concentration levels for each analyte of interest.

7.2.3 The calibration standards are prepared by spiking a blank Tenax or Tenax/charcoal trap with a methanolic solution of the calibration standards (including 50 ng of the internal standard, such as deuterated benzene), using the flash evaporation technique. The flash evaporation technique requires filling the needle of a 5.0 µL syringe with clean methanol and drawing air into the syringe to the 1.0 µL mark. This is followed by drawing a methanolic solution of the calibration standards (containing 25 µg/µL of the internal standard) to the 2.0 µL mark. The glass traps should be attached to the injection port of a gas chromatograph while maintaining the injector temperature at 160°C. The carrier gas flow through the traps should be maintained at about 50 mL/min.

7.2.4 After directing the gas flow through the trap, the contents of the syringe should be slowly expelled through the gas chromatograph injection port over about 15 sec. After 25 sec have elapsed, the gas flow through the trap should be shut off, the syringe removed, and the trap analyzed by the PTD-GC/MS procedure outlined in Method 8240. The total flow of gas through the traps during addition of calibration standards to blank cartridges, or internal standards to sample cartridges, should be 25 mL or less.

7.2.5 Analyze each calibration standard for both Tenax and Tenax/charcoal cartridges according to Section 7.3. Tabulate the area response of the characteristic ions of each analyte against the concentration of the internal standard and calculate the response factor (RF) for each compound, using Equation 1.

$$RF = A_s C_{is} / A_{is} C_s \qquad (1)$$

where:

A_s = Area of the characteristic ion for the analyte to be measured.

A_{is} = Area of the characteristic ion for the internal standard.

C_{is} = Amount (ng) of the internal standard.

C_s = Amount (ng) of the volatile POHC in calibration standard.

If the RF value over the working range is a constant (<10% RSD), the RF can be assumed to be invariant, and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} versus RF.

7.2.6 The working calibration curve or RF must be verified on each working day by the measurement of one or more of the calibration standards. If the response varies by more than ±25% for any analyte, a new calibration standard must be prepared and analyzed for that analyte.

7.3 The schematic of the PTD-GC/MS system is shown in Figure 1. The sample cartridge is placed in the thermal desorption apparatus (for Inside/Inside VOST cartridges, use Supelco "clamshell" heater; for Inside/Outside VOST cartridges, user fabricated unit is required) and desorbed in the purge-and-trap system by heating to 180°C for 10 min at a flow rate of 40 mL/min. The desorbed components pass into the bottom of the water column, are purged from the water, and collected on the analytical adsorbent trap. After the 10 min desorption period, the compounds are desorbed from the analytical adsorbent trap into the GC/MS system according to the procedures described in Method 8240.

7.4 Qualitative analysis

7.4.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

7.4.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine, where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time, will be accepted as meeting this criterion.

7.4.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.4.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.4.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.4.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra

containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.4.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of the sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

7.5 Quantitative analysis

7.5.1 When an analyte has been qualitatively identified, quantitation should be based on the integrated abundance from the EICP of the primary characteristic ion chosen for that analyte. If the sample produces an interference for the primary characteristic ion, a secondary characteristic ion should be used.

7.5.1.1 Using the internal standard calibration procedure, the amount of analyte in the sample cartridge is calculated using the response factor (RF) determined in Section 7.2.5 and Equation 2.

$$\text{Amount of POHC} = A_s C_{is} / A_{is} RF \qquad (2)$$

where:

A_s = Area of the characteristic ion for the analyte to be measured.

A_{is} = Area for the characteristic ion of the internal standard.

C_{is} = Amount (ng) of internal standard.

7.5.1.2 The choice of methods for evaluating data collected using VOST for incinerator trial burns is a regulatory decision. The procedures used extensively by one user are outlined below.

7.5.1.3 The total amount of the POHCs of interest collected on a pair of traps should be summed.

7.5.1.4 The observation of high concentrations of POHCs of interest in blank cartridges indicates possible residual contamination of the sorbent cartridges prior to shipment to and use at the site. Data that fall in this category (especially data indicating high concentrations of POHCs in blank sorbent cartridges) should be qualified with regard to validity, and blank data should be reported separately. The applicability of data of this type to the determination of DRE is a regulatory decision. Continued observation of high concentrations of POHCs in blank sorbent cartridges indicates that procedures for cleanup, monitoring, shipment, and storage of sorbent cartridges by a particular user be investigated to eliminate this problem.

7.5.1.5 If any internal standard recoveries fall outside the control limits established in Section 8.4, data for all analytes determined for that cartridge(s) must be qualified with the observation.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 0030 for sample preparation procedures.

8.2 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of blank Tenax and Tenax/charcoal cartridges spiked with the analytes of interest. The laboratory is required to maintain performance records to define the quality of

data that are generated. Ongoing performance checks must be compared with established performance criteria to determine if results are within the expected precision and accuracy limits of the method.

8.2.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable precision and accuracy with this method. This ability is established as described in Section 7.2.

8.2.2 The laboratory must spike all Tenax and Tenax/charcoal cartridges with the internal standard(s) to monitor continuing laboratory performance. This procedure is described in Section 7.2.

8.3 To establish the ability to generate acceptable accuracy and precision, the analyst must spike blank Tenax and Tenax/charcoal cartridges with the analytes of interest at two concentrations in the working range.

8.3.1 The average response factor ($\overline{RF}$) and the standard deviation (s) for each must be calculated.

8.3.2 The average recovery and standard deviation must fall within the expected range for determination of volatile POHCs using this method. The expected range for recovery of volatile POHCs using this method is 50-150%.

8.4 The analyst must calculate method performance criteria for the internal standard(s).

8.4.1 Calculate upper and lower control limits for method performances using the average area response (A) and standard deviation(s) for internal standard:

Upper Control Limit (UCL) = A + 3s
Lower Control Limit (LCL) = A - 3s

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance. The control limits must be replaced by method performance criteria as they become available from the U.S. EPA.

8.5 The laboratory is required to spike all sample cartridges (Tenax and Tenax/charcoal) with internal standard.

8.6 Each day, the analyst must demonstrate through analysis of blank Tenax and Tenax/charcoal cartridges and organic-free reagent water that interferences from the analytical system are under control.

8.7 The daily GC/MS performance tests required for this method are described in Method 8240.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. Protocol for Collection and Analysis of Volatile POHC's Using VOST. EPA/600/8-84-007, March 1984.

2. Validation of the Volatile Organic Sampling Train (VOST) Protocol. Volumes I and II. EPA/600/4-86-014a, January 1986.

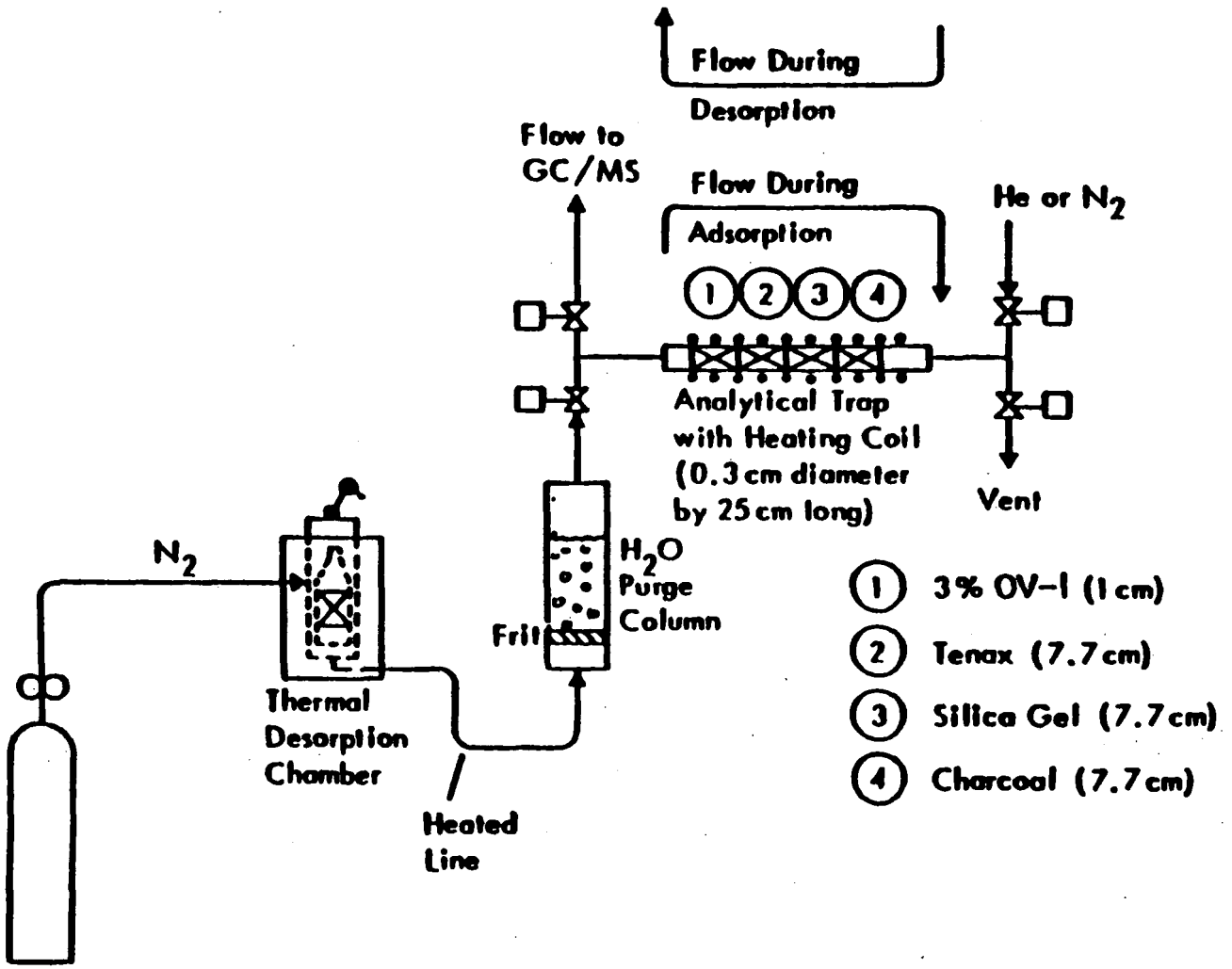
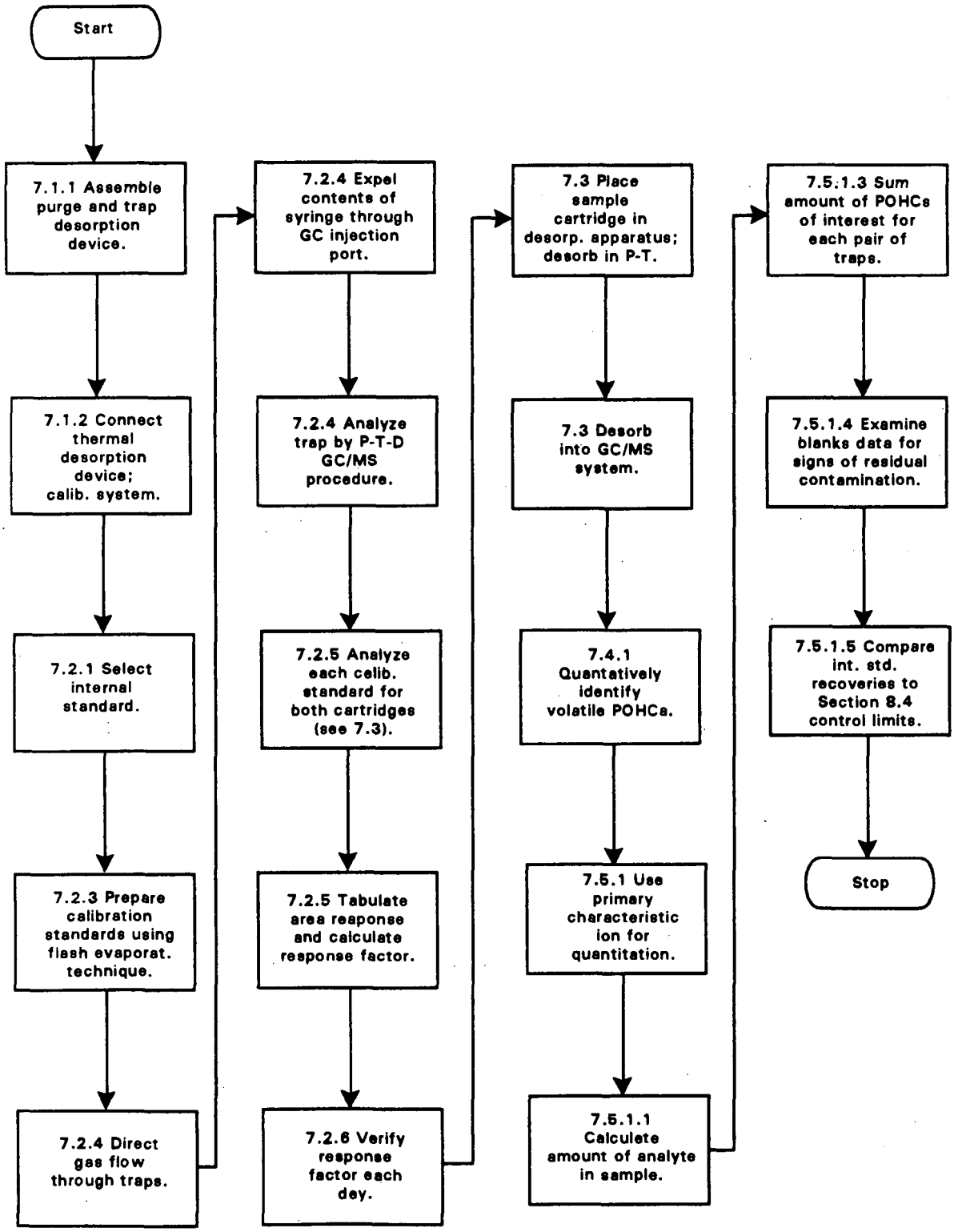


Figure 1. Schematic diagram of trap desorption/analysis system.

METHOD 5040A
ANALYSIS OF SORBENT CARTRIDGES FROM VOLATILE ORGANIC SAMPLING TRAIN (VOST): GAS CHROMATOGRAPHY/MASS SPECTROMETRY TECHNIQUE



METHOD 5041

PROTOCOL FOR ANALYSIS OF SORBENT CARTRIDGES FROM VOLATILE ORGANIC SAMPLING TRAIN (VOST): WIDE-BORE CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 This method describes the analysis of volatile principal organic hazardous constituents (POHCs) collected from the stack gas effluents of hazardous waste incinerators using the VOST methodology (1). For a comprehensive description of the VOST sampling methodology see Method 0030. The following compounds may be determined by this method:

Compound Name	CAS No.[a]
Acetone	67-64-1
Acrylonitrile	107-13-1
Benzene	71-43-2
Bromodichloromethane	75-27-4
Bromoform[b]	75-25-2
Bromomethane[c]	74-83-9
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chlorodibromomethane	124-48-1
Chloroethane[c]	75-00-3
Chloroform	67-66-3
Chloromethane[c]	74-87-3
Dibromomethane	74-95-3
1,1-Dichloroethane	75-35-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Ethylbenzene[b]	100-41-4
Iodomethane	74-88-4
Methylene chloride	75-09-2
Styrene[b]	100-42-5
1,1,2,2-Tetrachloroethane[b]	79-34-5
Tetrachloroethene	127-18-4
Toluene	108-88-3

(continued)

Compound Name	CAS No.[a]
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane[b]	96-18-4
Vinyl chloride[c]	75-01-4
Xylenes[b]	

[a] Chemical Abstract Services Registry Number.

[b] Boiling point of this compound is above 132°C. Method 0030 is not appropriate for quantitative sampling of this analyte.

[c] Boiling point of this compound is below 30°C. Special precautions must be taken when sampling for this analyte by Method 0030. Refer to Sec. 1.3 for discussion.

1.2 This method is most successfully applied to the analysis of non-polar organic compounds with boiling points between 30°C and 100°C. Data are applied to the calculation of destruction and removal efficiency (DRE), with limitations discussed below.

1.3 This method may be applied to analysis of many compounds which boil above 100°C, but Method 0030 is always inappropriate for collection of compounds with boiling points above 132°C. All target analytes with boiling points greater than 132°C are so noted in the target analyte list presented in Sec. 1.1. Use of Method 0030 for collection of compounds boiling between 100°C and 132°C is often possible, and must be decided based on case by case inspection of information such as sampling method collection efficiency, tube desorption efficiency, and analytical method precision and bias. An organic compound with a boiling point below 30°C may break through the sorbent under the conditions used for sample collection. Quantitative values obtained for compounds with boiling points below 30°C must be qualified, since the value obtained represents a minimum value for the compound if breakthrough has occurred. In certain cases, additional QC measures may have been taken during sampling very low boilers with Method 0030. This information should be considered during the data interpretation stage.

When Method 5041 is used for survey analyses, values for compounds boiling above 132°C may be reported and qualified since the quantity obtained represents a minimum value for the compound. These minimum values should not be used for trial burn DRE calculations or to prove insignificant risk.

1.4 The VOST analytical methodology can be used to quantitate volatile organic compounds that are insoluble or slightly soluble in water. When volatile, water soluble compounds are included in the VOST organic compound analyte list, quantitation limits can be expected to be approximately ten times

higher than quantitation limits for water insoluble compounds (if the compounds can be recovered at all) because the purging efficiency from water (and possibly from Tenax-GC®) is poor.

1.5 Overall sensitivity of the method is dependent upon the level of interferences encountered in the sample and the presence of detectable concentrations of volatile POHCs in blanks. The target detection limit of this method is 0.1 $\mu g/m^3$ (ng/L) of flue gas, to permit calculation of a DRE equal to or greater than 99.99% for volatile POHCs which may be present in the waste stream at 100 ppm. The upper end of the range of applicability of this method is limited by the dynamic range of the analytical instrumentation, the overall loading of organic compounds on the exposed tubes, and breakthrough of the volatile POHCs on the sorbent traps used to collect the sample. Table 1 presents retention times and characteristic ions for volatile compounds which can be determined by this method. Table 2 presents method detection limits for a range of volatile compounds analyzed by the wide-bore VOST methodology.

1.6 The wide-bore VOST analytical methodology is restricted to use by, or under the supervision of, analysts experienced in the use of sorbent media, purge-and-trap systems, and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

2.0 SUMMARY OF METHOD

2.1 The sorbent tubes are thermally desorbed by heating and purging with organic-free helium. The gaseous effluent from the tubes is bubbled through pre-purged organic-free reagent water and trapped on an analytical sorbent trap in a purge-and-trap unit (Figure 2). After desorption, the analytical sorbent trap is heated rapidly and the gas flow from the analytical trap is directed to the head of a wide-bore column under subambient conditions. The volatile organic compounds desorbed from the analytical trap are separated by temperature programmed high resolution gas chromatography and detected by continuously scanning low resolution mass spectrometry (Figure 3). Concentrations of volatile organic compounds are calculated from a multi-point calibration curve, using the method of response factors.

3.0 INTERFERENCES

3.1 Sorbent tubes which are to be analyzed for volatile organic compounds can be contaminated by diffusion of volatile organic compounds (particularly Freon® refrigerants and common organic solvents) through the external container (even through a Teflon® lined screw cap on a glass container) and the Swagelok® sorbent tube caps during shipment and storage. The sorbent tubes can also be contaminated if organic solvents are present in the analytical laboratory. The use of blanks is essential to assess the extent of any contamination. Field blanks must be prepared and taken to the field. The end caps of the tubes are removed for the period of time required to exchange two pairs of traps on the VOST sampling apparatus. The tubes are recapped and shipped and handled exactly as the actual field samples are shipped and handled. At least one pair of field blanks is included with each six pairs of sample cartridges collected.

3.2 At least one pair of blank cartridges (one Tenax-GC®, one Tenax-GC®/charcoal) shall be included with shipment of cartridges to a hazardous waste incinerator site as trip blanks. These trip blanks will be treated like field blanks except that the end caps will not be removed during storage at the site. This pair of traps will be analyzed to monitor potential contamination which may occur during storage and shipment.

3.3 Analytical system blanks are required to demonstrate that contamination of the purge-and-trap unit and the gas chromatograph/mass spectrometer has not occurred or that, in the event of analysis of sorbent tubes with very high concentrations of organic compounds, no compound carryover is occurring. Tenax® from the same preparation batch as the Tenax® used for field sampling should be used in the preparation of the method (laboratory) blanks. A sufficient number of cleaned Tenax® tubes from the same batch as the field samples should be reserved in the laboratory for use as blanks.

3.4 Cross contamination can occur whenever low-concentration samples are analyzed after high-concentration samples, or when several high-concentration samples are analyzed sequentially. When an unusually concentrated sample is analyzed, this analysis should be followed by a method blank to establish that the analytical system is free of contamination. If analysis of a blank demonstrates that the system is contaminated, an additional bake cycle should be used. If the analytical system is still contaminated after additional baking, routine system maintenance should be performed: the analytical trap should be changed and conditioned, routine column maintenance should be performed (or replacement of the column and conditioning of the new column, if necessary), and bakeout of the ion source (or cleaning of the ion source and rods, if required). After system maintenance has been performed, analysis of a blank is required to demonstrate that the cleanliness of the system is acceptable.

3.5 Impurities in the purge gas and from organic compounds out-gassing in tubing account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by analyzing two sets of clean, blank sorbent tubes with organic-free reagent purge water as system blanks. The analytical system is acceptably clean when these two sets of blank tubes show values for the analytes which are within one standard deviation of the normal system blank. Use of plastic coatings, non-Teflon® thread sealants, or flow controllers with rubber components should be avoided.

3.6 VOST tubes are handled in the laboratory to spike standards and to position the tubes within the desorption apparatus. When sorbent media are handled in the laboratory atmosphere, contamination is possible if there are organic solvents in use anywhere in the laboratory. It is therefore necessary to make daily use of system blanks to monitor the cleanliness of the sorbents and the absence of contamination from the analytical system. A single set of system blank tubes shall be exposed to normal laboratory handling procedures and analyzed as a sample. This sample should be within one standard deviation of normal VOST tube blanks to demonstrate lack of contamination of the sorbent media.

3.7 If the emission source has a high concentration of non-target organic compounds (for example, hydrocarbons at concentrations of hundreds of ppm), the

presence of these non-target compounds will interfere with the performance of the VOST analytical methodology. If one or more of the compounds of interest saturates the chromatographic and mass spectrometric instrumentation, no quantitative calculations can be made and the tubes which have been sampled under the same conditions will yield no valid data for any of the saturated compounds. In the presence of a very high organic loading, even if the compounds of interest are not saturated, the instrumentation is so saturated that the linear range has been surpassed. When instrument saturation occurs, it is possible that compounds of interest cannot even be identified correctly because a saturated mass spectrometer may mis-assign masses. Even if compounds of interest can be identified, accurate quantitative calculations are impossible at detector saturation. No determination can be made at detector saturation, even if the target compound itself is not saturated. At detector saturation, a negative bias will be encountered in analytical measurements and no accurate calculation can be made for the Destruction and Removal Efficiency if analytical values may be biased negatively.

3.8 The recoveries of the surrogate compounds, which are spiked on the VOST tubes immediately before analysis, should be monitored carefully as an overall indicator of the performance of the methodology. Since the matrix of stack emissions is so variable, only a general guideline for recovery of 50-150% can be used for surrogates. The analyst cannot use the surrogate recoveries as a guide for correction of compound recoveries. The surrogates are valuable only as a general indicator of correct operation of the methodology. If surrogates are not observed or if recovery of one or more of the surrogates is outside the 50-150% range, the VOST methodology is not operating correctly. The cause of the failure in the methodology is not obvious. The matrix of stack emissions contains large amounts of water, may be highly acidic, and may contain large amounts of target and non-target organic compounds. Chemical and surface interactions may be occurring on the tubes. If recoveries of surrogate compounds are extremely low or surrogate compounds cannot even be identified in the analytical process, then failure to observe an analyte may or may not imply that the compound of interest has been removed from the emissions with a high degree of efficiency (that is, the Destruction and Removal Efficiency for that analyte is high).

4.0 APPARATUS AND MATERIALS

4.1 Tube desorption apparatus: Acceptable performance of the methodology requires: 1) temperature regulation to ensure that tube temperature during desorption is regulated to 180°C $\pm$ 10°; 2) good contact between tubes and the heating apparatus to ensure that the sorbent bed is thoroughly and uniformly heated to facilitate desorption of organic compounds; and 3) gas-tight connections to the ends of the tubes to ensure flow of desorption gas through the tubes without leakage during the heating/desorption process. A simple clamshell heater which will hold tubes which are 3/4" in outer diameter will perform acceptably as a desorption apparatus.

4.2 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: a sample purge vessel, an analytical trap, and a desorber. Complete devices are commercially available from a variety of sources, or the separate components may be assembled. The cartridge thermal desorption

apparatus is connected to the sample purge vessel by 1/8" Teflon® tubing (unheated transfer line). The tubing which connects the desorption chamber to the sample purge vessel should be as short as is practical.

4.2.1 The sample purge vessel is required to hold 5 mL of organic-free reagent water, through which the gaseous effluent from the VOST tubes is routed. The water column should be at least 3 cm deep. The gaseous headspace between the water column and the analytical trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The sample purger shown in Figure 4 meets these requirements. Alternate sample purging vessels may be used if equivalent performance is demonstrated.

4.2.2 The analytical trap must be at least 25 cm and have an internal diameter of at least 0.105 in. The analytical trap must contain the following components:

2,6-diphenylene oxide polymer:	60/80 mesh, chromatograph grade (Tenax-GC®, or equivalent)
methyl silicone packing:	OV-1 (3%) on Chromosorb-W 60/80 mesh, or equivalent
silica gel:	35/60 mesh, Davison grade 15 or equivalent
coconut charcoal:	prepare from Barneby Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen.

The proportions are: 1/3 Tenax-GC®, 1/3 silica gel, and 1/3 charcoal, with approximately 1.0 cm of methyl silicone packing. The analytical trap should be conditioned for four hours at 180°C with gas flow (10 mL/min) prior to use in sample analysis. During conditioning, the effluent of the trap should not be vented to the analytical column. The thermal desorption apparatus is connected to the injection system of the mass spectrometer by a transfer line which is heated to 100°C.

4.2.3 The desorber must be capable of rapidly heating the analytical trap to 180°C for desorption. The polymer section of the trap should not exceed 180°C, and the remaining sections should not exceed 220°C, during bake-out mode.

4.3 Gas chromatograph/mass spectrometer/data system:

4.3.1 Gas chromatograph: An analytical system complete with a temperature programmable oven with sub-ambient temperature capabilities and all required accessories, including syringes, analytical columns, and gases.

4.3.2 Chromatographic column: 30 m x 0.53 mm ID wide-bore fused silica capillary column, 3 μm film thickness, DB-624 or equivalent.

4.3.3 Mass spectrometer: capable of scanning from 35-260 amu every second or less, using 70 eV (nominal) electron energy in the electron ionization mode and producing a mass spectrum that meets all of the criteria in Table 3 when 50 ng of 4-bromofluorobenzene (BFB) is injected into the water in the purge vessel.

4.3.4 Gas chromatograph/mass spectrometer interface: Any gas chromatograph to mass spectrometer interface that gives acceptable calibration points at 50 ng or less per injection of each of the analytes, and achieves the performance criteria for 4-bromofluorobenzene shown in Table 3, may be used. If a glass jet separator is used with the wide-bore column, a helium make-up flow of approximately 15 mL, introduced after the end of the column and prior to the entrance of the effluent to the separator, will be required for optimum performance.

4.3.5 Data system: A computer system that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any gas chromatographic/mass spectrometric data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows the integration of the ion abundances in any EICP between specified time or scan number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.4 Wrenches: 9/16", 1/2", 7/16", and 5/16".

4.5 Teflon® tubing: 1/8" diameter.

4.6 Syringes: 25 μL syringes (2), 10 μL syringes (2).

4.7 Fittings: 1/4" nuts, 1/8" nuts, 1/16" nuts, 1/4" to 1/8" union, 1/4" to 1/4" union, 1/4" to 1/16" union.

4.8 Adjustable stand to raise the level of the desorption unit, if required.

4.9 Volumetric flasks: 5 mL, class A with ground glass stopper.

4.10 Injector port or equivalent, heated to 180°C for loading standards onto VOST tubes prior to analysis.

4.11 Vials: 2 mL, with Teflon® lined screw caps or crimp tops.

4.12 Syringe: 5 mL, gas-tight with shutoff valve.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2.1 It is advisable to maintain the stock of organic-free reagent water generated for use in the purge-and-trap apparatus with a continuous stream of inert gas bubbled through the water. Continuous bubbling of the inert gas maintains a positive pressure of inert gas above the water as a safeguard against contamination.

5.3 Methanol, CH_3OH. Pesticide quality or equivalent. To avoid contamination with other laboratory solvents, it is advisable to maintain a separate stock of methanol for the preparation of standards for VOST analysis and to regulate the use of this methanol very carefully.

5.4 Stock standard solutions - Can be prepared from pure standard materials or can be purchased as certified solutions. Stock standard solutions must be prepared in high purity methanol. All preparation of standards should take place in a hood, both to avoid contamination and to ensure safety of the analyst preparing the standards.

5.4.1 Place about 4 mL of high purity methanol in a 5 mL volumetric flask. Allow the flask to stand, unstoppered, for about 10 min, or until all alcohol wetted surfaces have dried.

5.4.1.1 Add appropriate volumes of neat liquid chemicals or certified solutions, using a syringe of the appropriate volume. Liquid which is added to the volumetric flask must fall directly into the alcohol without contacting the neck of the flask. Gaseous standards can be purchased as methanol solutions from several commercial vendors.

5.4.1.2 Dilute to volume with high purity methanol, stopper, and then mix by inverting the flask several times. Calculate concentration by the dilution of certified solutions or neat chemicals.

5.4.2 Transfer the stock standard solution into a Teflon® sealed screw cap bottle. An amber bottle may be used. Store, with minimal headspace, at -10°C to -20°C, and protect from light.

5.4.3 Prepare fresh standards every two months for gases. Reactive compounds such as styrene may need to be prepared more frequently. All other standards must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.5 Secondary dilution standards: Using stock standard solutions, prepare, in high purity methanol, secondary dilution standards containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.6 Surrogate standards: The recommended surrogates are toluene-d_8, 4-bromofluorobenzene, and 1,2-dichloroethane-d_4. Other compounds may be used as surrogate compounds, depending upon the requirements of the analysis. Surrogate compounds are selected to span the elution range of the compounds of interest. Isotopically labeled compounds are selected to preclude the observation of the same compounds in the stack emissions. More than one surrogate is used so that surrogate measurements can still be made even if analytical interferences with one or more of the surrogate compounds are encountered. However, at least three surrogate compounds should be used to monitor the performance of the methodology. A stock surrogate compound solution in high purity methanol should be prepared as described in Sec. 5.4, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 250 μg/10 mL in high purity methanol. Each pair of VOST tubes (or each individual VOST tube, if the tubes are analyzed separately) must be spiked with 10 μL of the surrogate spiking solution prior to GC/MS analysis.

5.7 Internal standards: The recommended internal standards are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being analyzed by GC/MS. The internal standards should be distributed through the chromatographic elution range. Prepare internal standard stock and secondary dilution standards in high purity methanol using the procedures described in Secs. 5.2 and 5.3. The secondary dilution standard should be prepared at a concentration of 25 mg/L of each of the internal standard compounds. Addition of 10 μL of this internal standard solution to each pair of VOST tubes (or to each VOST tube, if the tubes are analyzed individually) is the equivalent of 250 ng total.

5.8 4-Bromofluorobenzene (BFB) standard: A standard solution containing 25 ng/μL of BFB in high purity methanol should be prepared for use as a tuning standard.

5.9 Calibration standards: Calibration standards at a minimum of five concentrations will be required from the secondary dilution of stock standards (see Secs. 5.2 and 5.3). A range of concentrations for calibration can be obtained by use of different volumes of a 50 mg/L methanol solution of the calibration standards. One of the concentrations used should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in field samples but should not exceed the linear range of the GC/MS analytical system (a typical range for a calibration would be 10, 50, 100, 350, and 500 ng, for example). Each calibration standard should contain each analyte for detection by this method. Store calibration standards for one week only in a vial with no headspace.

5.10 Great care must be taken to maintain the integrity of all standard solutions. All standards of volatile compounds in methanol must be stored at -10° to -20°C in amber bottles with Teflon® lined screw caps or crimp tops. In addition, careful attention must be paid to the use of syringes designated for a specific purpose or for use with only a single standard solution since cross contamination of volatile organic standards can occurs very readily.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Method 0030 for the VOST Sampling Methodology.

6.2 VOST samples are collected on paired cartridges. The first of the pair of sorbent cartridges is packed with approximately 1.6 g of Tenax-GC® resin. The second cartridge of the pair is packed with Tenax-GC® and petroleum based charcoal (3:1 by volume; approximately 1 g of each). In sampling, the emissions gas stream passes through the Tenax-GC® layer first and then through the charcoal layer. The Tenax-GC® is cleaned and reused; charcoal is not reused when tubes are prepared. Sorbent is cleaned and the tubes are packed. The tubes are desorbed and subjected to a blank check prior to being sent to the field. When the tubes are used for sampling (see Figure 5 for a schematic diagram of the Volatile Organic Sampling Train (VOST)), cooling water is circulated to the condensers and the temperature of the cooling water is maintained near 0°C. The end caps of the sorbent cartridges are placed in a clean, screw capped glass container during sample collection.

6.3 After the apparatus is leak checked, sample collection is accomplished by opening the valve to the first condenser, turning on the pump, and sampling at a rate of 1 liter/min for 20 minutes. The volume of sample for any pair of traps should not exceed 20 liters. An alternative set of conditions for sample collection requires sampling at a reduced flow rate, where the overall volume of sample collected is 5 liters at a rate of 0.25 L/min for 20 minutes. The 20 minute period is required for collecting an integrated sample.

6.4 Following collection of 20 liters of sample, the train is leak checked a second time at the highest pressure drop encountered during the run to minimize the chance of vacuum desorption of organics from the Tenax®.

6.5 The train is returned to atmospheric pressure and the two sorbent cartridges are removed. The end caps are replaced and the cartridges are placed in a suitable environment for storage and transport until analysis. The sample is considered invalid if the leak test does not meet specifications.

6.6 A new pair of cartridges is placed in the VOST, the VOST is leak checked, and the sample collection process is repeated until six pairs of traps have been exposed.

6.7 All sample cartridges are kept in coolers on cold packs after exposure and during shipment. Upon receipt at the laboratory, the cartridges are stored in a refrigerator at 4°C until analysis.

7.0 PROCEDURE

7.1 Recommended operating conditions for cartridge desorber, purge-and-trap unit, and gas chromatograph/mass spectrometer using the wide-bore column are:

<u>Cartridge Desorption Oven</u>	
Desorb Temperature	180°C
Desorb Time	11 minutes
Desorption Gas Flow	40 mL/min
Desorption/Carrier Gas	Helium, Grade 5.0
<u>Purge-and-Trap Concentrator</u>	
Analytical Trap Desorption Flow	2.5 mL/min helium
Purge Temperature	Ambient
Purge Time	11 minutes
Analytical Trap Desorb Temperature	180°C
Analytical Trap Desorb Time	5 minutes
<u>Gas Chromatograph</u>	
Column	DB-624, 0.53 mm ID x 30 m thick film (3 μm) fused silica capillary, or equivalent
Carrier Gas Flow	15 mL/min
Makeup Gas Flow	15 mL/min
Injector Temperature	200°C
Transfer Oven Temperature	240°C
Initial Temperature	5°C
Initial Hold Time	2 minutes
Program Rate	6°C/min
Final Temperature	240°C
Final Hold Time	1 minute, or until elution ceases
<u>Mass Spectrometer</u>	
Manifold Temperature	105°C
Scan Rate	1 sec/cycle
Mass Range	35-260 amu
Electron Energy	70 eV (nominal)
Source Temperature	According to manufacturer's specifications

7.2 Each GC/MS system must be hardware tuned to meet the criteria in Table 3 for a 50 ng injection of 4-bromofluorobenzene (2 μL injection of the BFB standard solution into the water of the purge vessel). No analyses may be initiated until the criteria presented in Table 3 are met.

7.3 Assemble a purge-and-trap device that meets the specifications in Method 5030. Condition the analytical trap overnight at 180°C in the purge mode, with an inert gas flow of at least 20 mL/min. Prior to use each day, condition the trap for 10 minutes by backflushing at 180°C, with the column at 220°C.

7.4 Connect the purge-and-trap device to a gas chromatograph.

7.5 Assemble a VOST tube desorption apparatus which meets the requirements of Sec. 4.1.

7.6 Connect the VOST tube desorption apparatus to the purge-and-trap unit.

7.7 Calibrate the instrument using the internal standard procedure, with standards and calibration compounds spiked onto cleaned VOST tubes for calibration.

7.7.1 Compounds in methanolic solution are spiked onto VOST tubes using the flash evaporation technique. To perform flash evaporation, the injector of a gas chromatograph or an equivalent piece of equipment is required.

7.7.1.1 Prepare a syringe with the appropriate volume of methanolic standard solution (either surrogates, internal standards, or calibration compounds).

7.7.1.2 With the injector port heated to 180°C, and with an inert gas flow of 10 mL/min through the injector port, connect the paired VOST tubes (connected as in Figure 1, with gas flow in the same direction as the sampling gas flow) to the injector port; tighten with a wrench so that there is no leakage of gas. If separate tubes are being analyzed, an individual Tenax® or Tenax®/charcoal tube is connected to the injector.

7.7.1.3 After directing the gas flow through the VOST tubes, slowly inject the first standard solution over a period of 25 seconds. Wait for 5 sec before withdrawing the syringe from the injector port.

7.7.1.4 Inject a second standard (if required) over a period of 25 seconds and wait for 5 sec before withdrawing the syringe from the injector port.

7.7.1.5 Repeat the sequence above as required until all of the necessary compounds are spiked onto the VOST tubes.

7.7.1.6 Wait for 30 seconds, with gas flow, after the last spike before disconnecting the tubes. The total time the tubes are connected to the injector port with gas flow should not exceed 2.5 minutes. Total gas flow through the tubes during the spiking process should not exceed 25 mL to prevent break through of adsorbed compounds during the spiking process. To allow more time for connecting and disconnecting tubes, an on/off valve may be installed in the gas line to the injector port so that gas is not flowing through the tubes during the connection/disconnection process.

7.8 Prepare the purge-and-trap unit with 5 mL of organic-free reagent water in the purge vessel.

7.9 Connect the paired VOST tubes to the gas lines in the tube desorption unit. The tubes must be connected so that the gas flow during desorption will be opposite to the flow of gas during sampling: i.e., the tube desorption gas passes through the charcoal portion of the tube first. An on/off valve may be installed in the gas line leading to the tube desorption unit in order to prevent flow of gas through the tubes during the connection process.

7.10 Initiate tube desorption/purge and heating of the VOST tubes in the desorption apparatus.

7.11 Set the oven of the gas chromatograph to subambient temperatures by cooling with liquid nitrogen.

7.12 Prepare the GC/MS system for data acquisition.

7.13 At the conclusion of the tube/water purge time, attach the analytical trap to the gas chromatograph, adjust the purge-and-trap device to the desorb mode, and initiate the gas chromatographic program and the GC/MS data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the analytical trap to 180°C while backflushing the trap with inert gas at 2.5 mL/min for 5 min. Initiate the program for the gas chromatograph and simultaneously initiate data acquisition on the GC/MS system.

7.14 While the analytical trap is being desorbed into the gas chromatograph, empty the purging vessel. Wash the purging vessel with a minimum of two 5 mL flushes of organic-free reagent water (or methanol followed by organic-free reagent water) to avoid carryover of analytes into subsequent analyses.

7.15 After the sample has been desorbed, recondition the analytical trap by employing a bake cycle on the purge-and-trap unit. The analytical trap may be baked at temperatures up to 220°C. However, extensive use of high temperatures to recondition the trap will shorten the useful life of the analytical trap. After approximately 11 minutes, terminate the trap bake and cool the trap to ambient temperatures in preparation for the next sample. This procedure is a convention for reasonable samples and should be adequate if the concentration of contamination does not saturate the analytical system. If the organic compound concentration is so high that the analytical system is saturated beyond the point where even extended system bakeout is not sufficient to clean the system, a more extensive system maintenance must be performed. To perform extensive system maintenance, the analytical trap is replaced and the new trap is conditioned. Maintenance is performed on the GC column by removing at least one foot from the front end of the column. If the chromatography does not recover after column maintenance, the chromatographic column must be replaced. The ion source should be baked out and, if the bakeout is not sufficient to restore mass spectrometric peak shape and sensitivity, the ion source and the quadrupole rods must be cleaned.

7.16 Initial calibration for the analysis of VOST tubes: It is essential that calibration be performed in the mode in which analysis will be performed. If tubes are being analyzed as pairs, calibration standards should be prepared

on paired tubes. If tubes are being analyzed individually, a calibration should be performed on individual Tenax® only tubes and Tenax®/charcoal tubes.

7.16.1 Prepare the calibration standards by spiking VOST tubes using the procedure described in Sec. 7.7.1. Spike each pair of VOST tubes (or each of the individual tubes) immediately before analysis. Perform the calibration analyses in order from low concentration to high to minimize the compound carryover. Add 5.0 mL of organic-free reagent water to the purging vessel. Initiate tube desorb/purge according to the procedure described above.

7.16.2 Tabulate the area response of the characteristic primary ions (Table 1) against concentration for each target compound, each surrogate compound, and each internal standard. The first criterion for quantitative analysis is correct identification of compounds. The compounds must elute within $\pm$ 0.06 retention time units of the elution time of the standard analyzed on the same analytical system on the day of the analysis. The analytes should be quantitated relative to the closest eluting internal standard, according to the scheme shown in Table 4. Calculate response factors (RF) for each compound relative to the internal standard shown in Table 4. The internal standard selected for the calculation of RF is the internal standard that has a retention time closest to the compound being measured. The RF is calculated as follows:

$$RF = (A_x/C_{is})/(A_{is}/C_x)$$

where:

A_x = area of the characteristic ion for the compound being measured.

A_{is} = area of the characteristic ion for the specific internal standard.

C_{is} = concentration of the specific internal standard.

C_x = concentration of the compound being measured.

7.16.3 The average RF must be calculated for each compound. A system performance check should be made before the calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. The minimum acceptable average RF for these compounds should be 0.300 (0.250 for bromoform). These compounds typically have RFs of 0.4 - 0.6, and are used to check compound instability and check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

7.16.3.1 Chloromethane: This compound is the most likely compound to be lost if the purge flow is too fast.

7.16.3.2 Bromoform: This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in transfer lines may adversely affect response. Response of the primary quantitation ion (m/z 173) is directly affected by the tuning for 4-bromofluorobenzene at the ions of masses 174 and 176. Increasing the ratio of ions 174 and 176 to mass 95 (the base peak of the mass spectrum of bromofluorobenzene) may improve bromoform response.

7.16.3.3 1,1,2,2-Tetrachloroethane and 1,1-dichloroethane: These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.16.4 Using the response factors from the initial calibration, calculate the percent relative standard deviation (%RSD) for the Calibration Check Compounds (CCCs).

$$\%RSD = (SD/\bar{X}) \times 100$$

where:

%RSD = percent relative standard deviation

RF_i = individual RF measurement

$\overline{RF}$ = mean of 5 initial RFs for a compound (the 5 points over the calibration range)

SD = standard deviation of average RFs for a compound, where SD is calculated:

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(RF_i - \overline{RF})^2}{N-1}}$$

The %RSD for each individual CCC should be less than 30 percent. This criterion must be met in order for the individual calibration to be valid. The CCCs are: 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, and vinyl chloride.

7.17 Daily GC/MS Calibration

7.17.1 Prior to the analysis of samples, purge 50 ng of the 4-bromofluorobenzene standard. The resultant mass spectrum for the BFB must meet all of the criteria given in Table 3 before sample analysis begins. These criteria must be demonstrated every twelve hours of operation.

7.17.2 The initial calibration curve (Sec. 7.16) for each compound of interest must be checked and verified once every twelve hours of analysis time. This verification is accomplished by analyzing a

calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS and checking the SPCC (Sec. 7.16.3) and CCC (Sec. 7.16.4).

7.17.3 System Performance Check Compounds (SPCCs): A system performance check must be made each twelve hours of analysis. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not achieved, the system must be evaluated, and corrective action must be taken before analysis is allowed to begin. The minimum response factor for volatile SPCCs is 0.300 (0.250 for bromoform). If these minimum response factors are not achieved, some possible problems may be degradation of the standard mixture, contamination of the injector port, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. If the problem is active sites at the front end of the analytical column, column maintenance (removal of approximately 1 foot from the front end of the column) may remedy the problem.

7.17.4 Calibration Check Compounds: After the system performance check has been met, CCCs listed in Sec. 7.16.4 are used to check the validity of the initial calibration. Calculate the percent difference using the following equation:

$$\% \text{ Difference} = \frac{(RF_i - RF_c) \times 100}{RF_i}$$

where:

RF_i = average response factor from initial calibration

RF_c = response factor from current calibration check standard.

If the percent difference for any compound is greater than 20, the laboratory should consider this a warning limit. Benzene, toluene, and styrene will have problems with response factors if Tenax® decomposition occurs (either as a result of sampling exposure or temperature degradation), since these compounds are decomposition products of Tenax®. If the percent difference for each CCC is less than 25%, the initial calibration is assumed to be valid. If the criterion of percent difference less than 25% is not met for any one CCC, corrective action MUST be taken. Problems similar to those listed under SPCCs could affect this criterion. If a source of the problem cannot be determined after corrective action is taken, a new five-point calibration curve MUST be generated. The criteria for the CCCs MUST be met before quantitative analysis can begin.

7.17.5 Internal standard responses and retention times in the check calibration standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the last check calibration (12 hr), the chromatographic system must be inspected for malfunctions and corrections

must be made, as required. A factor which may influence the retention times of the internal standards on sample tubes is the level of overall organic compound loading on the VOST tubes. If the VOST tubes are very highly loaded with either a single compound or with multiple organic compounds, retention times for standards and compounds of interest will be affected. If the area for the primary ion of any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration check, the gas chromatograph and mass spectrometer should be inspected for malfunctions and corrections must be made, as appropriate. If the level of organic loading of samples is high, areas for the primary ions of both compounds of interest and standards will be adversely affected. Calibration check standards should not be subject to variation, since the concentrations of organic compounds on these samples are set to be within the linear range of the instrumentation. If instrument malfunction has occurred, analyses of samples performed under conditions of malfunction may be invalidated.

7.18 GC/MS Analysis of Samples

7.18.1 Set up the cartridge desorption unit, purge-and-trap unit, and GC/MS as described above.

7.18.2 BFB tuning criteria and daily GC/MS calibration check criteria must be met before analyzing samples.

7.18.3 Adjust the helium purge gas flow rate (through the cartridges and purge vessel) to approximately 40 mL/min. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. A flow rate which is too high reduces the recovery of chloromethane, and an insufficient gas flow rate reduces the recovery of bromoform.

7.18.4 The first analysis performed after the tuning check and the calibration or daily calibration check is a method blank. The method blank consists of clean VOST tubes (both Tenax® and Tenax®/charcoal) which are spiked with surrogate compounds and internal standards according to the procedure described in Sec. 7.7.1. The tubes which are used for the method blanks should be from the same batch of sorbent as the sorbent used for the field samples. After the tubes are cleaned and prepared for shipment to the field, sufficient pairs of tubes should be retained from the same batch in the laboratory to provide method blanks during the analysis.

7.18.5 The organic-free reagent water for the purge vessel for the analysis of each of the VOST samples should be supplied from the laboratory inventory which is maintained with constant bubbling of inert gas to avoid contamination.

7.18.6 If the analysis of a pair of VOST tubes has a concentration of analytes that exceeds the initial calibration range, no reanalysis of desorbed VOST tubes is possible. An additional calibration point can be added to bracket the higher concentration encountered in the samples so that the calibration database encompasses six or more points.

Alternatively, the data may be flagged in the report as "extrapolated beyond the upper range of the calibration." The use of the secondary ions shown in Table 1 is permissible only in the case of interference with the primary quantitation ion. Use of secondary ions to calculate compound concentration in the case of saturation of the primary ion is not an acceptable procedure, since a negative bias of an unpredictable magnitude is introduced into the quantitative data when saturation of the mass spectrum of a compound is encountered. If high organic loadings, either of a single compound or of multiple compounds, are encountered, it is vital that a method blank be analyzed prior to the analysis of another sample to demonstrate that no compound carryover is occurring. If concentrations of organic compounds are sufficiently high that carryover problems are profound, extensive bakeout of the purge-and-trap unit will be required. Complete replacement of the contaminated analytical trap, with the associated requirement for conditioning the new trap, may also be required for VOST samples which show excessive concentrations of organic compounds. Other measures which might be required for decontamination of the analytical system include bakeout of the mass spectrometer, replacement of the filament of the mass spectrometer, cleaning of the ion source of the mass spectrometer, and/or (depending on the nature of the contamination) maintenance of the chromatographic column or replacement of the chromatographic column, with the associated requirement for conditioning the new chromatographic column.

7.19 Data Interpretation

7.19.1 Qualitative analysis:

7.19.1.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

7.19.1.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound specific retention time will be accepted as meeting this criterion.

7.19.1.1.2 The RRT of the sample component is $\pm$ 0.06 RRT units of the RRT of the standard component.

7.19.1.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the

reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.19.1.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.19.1.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.19.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

7.19.2 Quantitative analysis:

7.19.2.1 When a compound has been identified, the quantitative analysis of that compound will be based on the integrated abundance from the extracted ion current profile of the primary characteristic ion for that compound (Table 1). In the event that there is interference with the primary ion so that quantitative measurements cannot be made, a secondary ion may be used.

NOTE: Use of a secondary ion to perform quantitative calculations in the event of the saturation of the primary ion is not an acceptable procedure because of the unpredictable extent of the negative bias which is introduced. Quantitative calculations are performed using the internal standard technique. The internal standard used to perform quantitative calculations shall be the internal standard nearest the retention time of a given analyte (see Table 4).

7.19.2.2 Calculate the amount of each identified analyte from the VOST tubes as follows:

$$\text{Amount (ng)} = (A_s C_{is})/(A_{is} RF)$$

where:

A_s = area of the characteristic ion for the analyte to be measured.

A_{is} = area of the characteristic ion of the internal standard.

C_{is} = amount (ng) of the internal standard.

7.19.2.3 The choice of methods for evaluating data collected using the VOST methodology for incinerator trial burns is a regulatory decision. Various procedures are used to decide whether blank correction should be performed and how blank correction should be performed. Regulatory agencies to which VOST data are submitted also vary in their preferences for data which are or which are not blank corrected.

7.19.2.4 The total amount of the POHCs of interest collected on a pair of traps should be summed.

7.19.2.5 The occurrence of high concentrations of analytes on method blank cartridges indicates possible residual contamination of sorbent cartridges prior to shipment and use at the sampling site. Data with high associated blank values must be qualified with respect to validity, and all blank data should be reported separately. No blank corrections should be made in this case. Whether or not data of this type can be applied to the determination of destruction and removal efficiency is a regulatory decision. Continued observation of high concentrations of analytes on blank sorbent cartridges indicates that procedures for cleanup and quality control for the sampling tubes are inadequate. Corrective action MUST be applied to tube preparation and monitoring procedures to maintain method blank concentrations below detection limits for analytes.

7.19.2.6 Where applicable, an estimate of concentration for noncalibrated components in the sample may be made. The formulae for quantitative calculations presented above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the Response Factor for the noncalibrated compound should be assumed to be 1. The nearest eluting internal standard free from interferences in the total ion chromatogram should be used to determine the concentration. The concentration which is obtained should be reported indicating: (1) that the value is an estimate; and (2) which internal standard was used.

7.19.2.7 If any internal standard recoveries fall outside the control limits established in Sec. 8.4, data for all analytes determined for that cartridge(s) must be qualified with the observation. Report results without correction for surrogate compound recovery data. When duplicates are analyzed, report the data obtained with the sample results.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum quality control requirements are specified in Chapter One. In addition, this program should consist of an initial demonstration of laboratory capability and an ongoing analysis of check samples to evaluate and document data quality. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When sample analyses indicate atypical method performance, a quality control check standard (spiked method blank) must be analyzed to confirm that the measurements were performed in an in-control mode of instrument operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank (laboratory blank sorbent tubes, reagent water purge) that interferences from the analytical system, glassware, sorbent tube preparation, and reagents are under control. Each time a new batch of

sorbent tubes is analyzed, a method blank should be processed as a safeguard against chronic laboratory contamination. Blank tubes which have been carried through all the stages of sorbent preparation and handling should be used in the analysis.

8.3 The experience of the analyst performing the GC/MS analyses is invaluable to the success of the analytical methods. Each day that the analysis is performed, the daily calibration check standard should be evaluated to determine if the chromatographic and tube desorption systems are operating properly. Questions that should be asked are: Do the peaks look normal? Is the system response obtained comparable to the response from previous calibrations? Careful examination of the chromatogram of the calibration standard can indicate whether column maintenance is required or whether the column is still usable, whether there are leaks in the system, whether the injector septum requires replacing, etc. If changes are made to the system (such as change of a column), a calibration check must be carried out and a new multipoint calibration must be generated.

8.4 Required instrument quality control is found in the following sections:

8.4.1 The mass spectrometer must be tuned to meet the specifications for 4-bromofluorobenzene in Sec. 7.2 (Table 3).

8.4.2 An initial calibration of the tube desorption/purge-and-trap/GC/MS must be performed as specified in Sec. 7.7.

8.4.3 The GC/MS system must meet the SPCC criteria specified in Sec. 7.16.3 and the CCC criteria in Sec. 7.16.4 each twelve hours of instrument operation.

8.5 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.5.1 A quality control (QC) check sample concentrate is required containing each analyte at a concentration of 10 mg/L in high purity methanol. The QC check sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If the QC check sample concentrate is prepared by the laboratory, the QC check sample concentrate must be prepared using stock standards prepared independently from the stock standards used for calibration.

8.5.2 Spike four pairs of cleaned, prepared VOST tubes with 10 μL of the QC check sample concentrate and analyze these spiked VOST tubes according to the method beginning in Sec. 7.0.

8.5.3 Calculate the average recovery (X) in ng and the standard deviation of the recovery (s) in ng for each analyte using the results of the four analyses.

8.5.4 The average recovery and standard deviation must fall within the expected range for determination of volatile organic compounds using the VOST analytical methodology. The expected range for recovery of

volatile organic compounds using this method is 50-150%. Standard deviation will be compound dependent, but should, in general, range from 15 to 30 ng. More detailed method performance criteria must be generated from historical records in the laboratory or from interlaboratory studies coordinated by the Environmental Protection Agency. Since the additional steps of sorbent tube spiking and desorption are superimposed upon the methodology of Method 8260, direct transposition of Method 8260 criteria is questionable. If the recovery and standard deviation for all analytes meet the acceptance criteria, the system performance is acceptable and the analysis of field samples may begin. If any individual standard deviation exceeds the precision limit or any individual recovery falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes listed in Table 1 presents a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes for this method are determined.

8.5.5 When one or more of the analytes tested fails at least one of the acceptance criteria, the analyst must proceed according to one of the alternatives below.

8.5.5.1 Locate and correct the source of any problem with the methodology and repeat the test for all the analytes beginning with Sec. 8.5.2.

8.5.5.2 Beginning with Sec. 8.5.2, repeat the test only for those analytes that have failed to meet acceptance criteria. Repeated failure, however, will confirm a general problem either with the measurement system or with the applicability of the methodology to the particular analyte (especially if the analyte in question is not listed in Table 1). If the problem is identified as originating in the measurement system, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Sec. 8.5.2.

8.6 To determine acceptable accuracy and precision limits for surrogate standards, the following procedure should be performed.

8.6.1 For each sample analyzed, calculate the percent recovery of each surrogate compound in the sample.

8.6.2 Once a minimum of thirty samples has been analyzed, calculate the average percent recovery (p) and the standard deviation of the percent recovery (s) for each of the surrogate compounds.

8.6.3 Calculate the upper and lower control limits for method performance for each surrogate standard. This calculation is performed as follows:

Upper Control Limit (UCL) = $p + 3s$
Lower Control Limit (LCL) = $p - 3s$

For reference, the comparable control limits for recovery of the surrogate compounds from water and soil in Method 8240 are:

4-Bromofluorobenzene	Water:	86-115%	Soil:	74-121%
1,2-Dichloroethane-d_4	Water:	76-114%	Soil:	70-121%
Toluene-d_8	Water:	88-110%	Soil:	81-117%

The control limits for the VOST methodology would be expected to be similar, but exact data are not presently available. Individual laboratory control limits can be established by the analysis of replicate samples.

8.6.4 If surrogate recovery is not within the limits established by the laboratory, the following procedures are required: (1) Verify that there are no errors in calculations, preparation of surrogate spiking solutions, and preparation of internal standard spiking solutions. Also, verify that instrument performance criteria have been met. (2) Recalculate the data and/or analyze a replicate sample, if replicates are available. (3) If all instrument performance criteria are met and recovery of surrogates from spiked blank VOST tubes (analysis of a method blank) is acceptable, the problem is due to the matrix. Emissions samples may be highly acidic and may be highly loaded with target and non target organic compounds. Both of these conditions will affect the ability to recover surrogate compounds which are spiked on the field samples. The surrogate compound recovery is thus a valuable indicator of the interactions of sampled compounds with the matrix. If surrogates spiked immediately before analysis cannot be observed with acceptable recovery, the implications for target organic analytes which have been sampled in the field must be assessed very carefully. If chemical or other interactions are occurring on the exposed tubes, the failure to observe an analyte may not necessarily imply that the Destruction and Removal Efficiency for that analyte is high.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples analyzed. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column or a different ionization mode using a mass spectrometer may be used, if replicate samples showing the same compound are available. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined in Chapter One. The MDL concentrations listed in Table 2 were obtained using cleaned blanked VOST tubes and reagent water. Similar results have been achieved with field samples. The MDL actually achieved in a given analysis will vary depending upon instrument sensitivity and the effects of the matrix. Preliminary spiking studies indicate that under these conditions, the method detection limit for spiked compounds in extremely complex matrices may be larger by a factor of 500-1000.

10.0 REFERENCES

1. Protocol for Collection and Analysis of Volatile POHCs Using VOST. EPA/600/8-84-007, March, 1984.

2. Validation of the Volatile Organic Sampling Train (VOST) Protocol. Volumes I and II. EPA/600/4-86-014A, January, 1986.

3. U. S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for Analysis of Pollutants Under the Clean Water Act, Method 624," October 26, 1984.

4. Bellar, T. A., and J. J. Lichtenberg, J. Amer. Water Works Assoc., 66(12), 739-744, 1974.

5. Bellar, T. A., and J. J. Lichtenberg, "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds," in Van Hall, ed., Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp 108-129, 1979.

TABLE 1.
RETENTION TIMES AND CHARACTERISTIC IONS FOR VOLATILE COMPOUNDS
WHICH CAN BE ANALYZED BY METHOD 5041

Compound	Retention Time (min)	Primary Ion Mass	Secondary Ion(s) Mass(es)
Acetone	7.1	43	58
Acrylonitrile	8.6	53	52, 51
Benzene	13.3	78	52, 77
Bromochloromethane	12.0	128	49, 130, 51
Bromodichloromethane	16.0	83	85, 129
4-Bromofluorobenzene	23.4	95	174, 176
Bromoform	22.5	173	171, 175, 252
Bromomethane	4.1	94	96, 79
Carbon disulfide	7.1	76	78
Carbon tetrachloride	12.6	117	119, 121
Chlorobenzene	20.5	112	114, 77
Chlorodibromomethane	19.3	129	208, 206
Chloroethane	4.2	64	66, 49
Chloroform	12.2	83	85, 47
Chloromethane	3.0	50	52, 49
Dibromomethane	15.4	93	174, 95
1,1-Dichloroethane	10.0	63	65, 83
1,2-Dichloroethane	13.3	62	64, 98
1,1-Dichloroethene	6.4	96	61, 98
trans-1,2-Dichloroethene	8.6	96	61, 98
1,2-Dichloropropane	15.2	63	62, 41
cis-1,3-Dichloropropene	17.0	75	77, 39
trans-1,3-Dichloropropene	18.2	75	77, 39
1,4-Difluorobenzene	14.2	114	63, 88
Ethylbenzene	21.1	106	91
Iodomethane	7.0	142	127, 141
Methylene chloride	8.1	84	49, 51, 86
Styrene	22.3	104	78, 103
1,1,2,2-Tetrachloroethane	24.0	83	85, 131, 133
Tetrachloroethene	18.6	164	129, 131, 166
Toluene	17.4	92	91, 65
1,1,1-Trichloroethane	12.4	97	99, 117
1,1,2-Trichloroethane	18.4	97	83, 85, 99
Trichloroethene	14.5	130	95, 97, 132
Trichlorofluoromethane	5.1	101	103, 66
1,2,3-Trichloropropane	24.0	75	110, 77, 61
Vinyl chloride	3.2	62	64, 61
Xylenes*	22.2	106	91

* The retention time given is for m- and p-xylene, which coelute on the wide-bore column. o-Xylene elutes approximately 50 seconds later.

TABLE 2.
PRELIMINARY METHOD DETECTION LIMITS AND BOILING POINTS
FOR VOLATILE ORGANICS ANALYZED BY METHOD 5041*

Compound	CAS Number	Detection Limit, ng	Boiling Point, °C
Chloromethane	74-87-3	58	-24
Bromomethane	74-83-9	26	4
Vinyl chloride	75-01-4	14	-13
Chloroethane	75-00-3	21	13
Methylene chloride	75-09-2	9	40
Acetone	67-64-1	35	56
Carbon disulfide	75-15-0	11	46
1,1-Dichloroethene	75-35-4	14	32
1,1-Dichloroethane	75-35-3	12	57
trans-1,2-Dichloroethene	156-60-5	11	48
Chloroform	67-66-3	11	62
1,2-Dichloroethane	107-06-2	13	83
1,1,1-Trichloroethane	71-55-6	8	74
Carbon tetrachloride	56-23-5	8	77
Bromodichloromethane	75-27-4	11	88
1,1,2,2-Tetrachloroethane**	79-34-5	23	146
1,2-Dichloropropane	78-87-5	12	95
trans-1,3-Dichloropropene	10061-02-6	17	112
Trichloroethene	79-01-6	11	87
Dibromochloromethane	124-48-1	21	122
1,1,2-Trichloroethane	79-00-5	26	114
Benzene	71-43-2	26	80
cis-1,3-Dichloropropene	10061-01-5	27	112
Bromoform**	75-25-2	26	150
Tetrachloroethene	127-18-4	11	121
Toluene	108-88-3	15	111
Chlorobenzene	108-90-7	15	132
Ethylbenzene**	100-41-4	21	136
Styrene**	100-42-5	46	145
Trichlorofluoromethane	75-69-4	17	24
Iodomethane	74-88-4	9	43
Acrylonitrile	107-13-1	13	78
Dibromomethane	74-95-3	14	97
1,2,3-Trichloropropane**	96-18-4	37	157
total Xylenes**		22	138-144

* The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. The detection limits cited above were determined according to Title 40 CFR, Part 136, Appendix B, using standards spiked onto clean VOST tubes. Since clean VOST tubes were used, the values cited above represent the best that the methodology can achieve. The presence of an emissions matrix will affect the ability of the methodology to perform at its optimum level.

** Not appropriate for quantitative sampling by Method 0030.

TABLE 3.
KEY ION ABUNDANCE CRITERIA FOR 4-BROMOFLUOROBENZENE

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95%, but less than 101% of mass 174
177	5 to 9% of mass 176

TABLE 4.
VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES
ASSIGNED FOR QUANTITATION

Bromochloromethane	1,4-Difluorobenzene
Acetone	Benzene
Acrylonitrile	Bromodichloromethane
Bromomethane	Bromoform
Carbon disulfide	Carbon tetrachloride
Chloroethane	Chlorodibromomethane
Chloroform	Dibromomethane
Chloromethane	1,2-Dichloropropane
1,1-Dichloroethane	cis-1,3-Dichloropropene
1,2-Dichloroethane	trans-1,3-Dichloropropene
1,2-Dichloroethane-d_4 (surrogate)	1,1,1-Trichloroethane
1,1-Dichloroethene	1,1,2-Trichloroethane
Trichloroethene	
trans-1,2-Dichloroethene	
Iodomethane	
Methylene chloride	
Trichlorofluoromethane	
Vinyl chloride	

Chlorobenzene-d5
4-Bromofluorobenzene (surrogate)
Chlorobenzene
Ethylbenzene
Styrene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
Toluene-d_8 (surrogate)
1,2,3-Trichloropropane
Xylenes

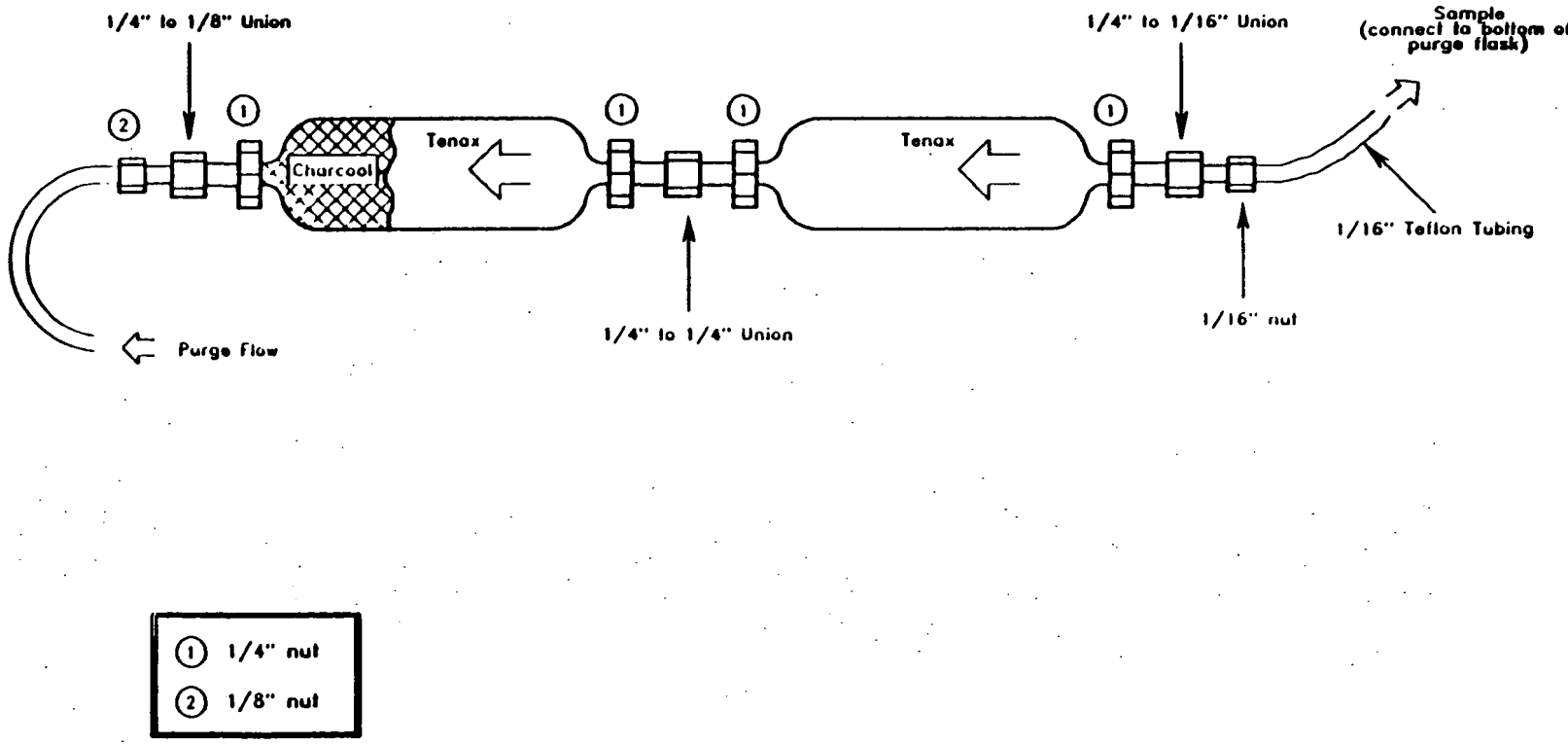


Figure 1. Cartridge Desorption Flow

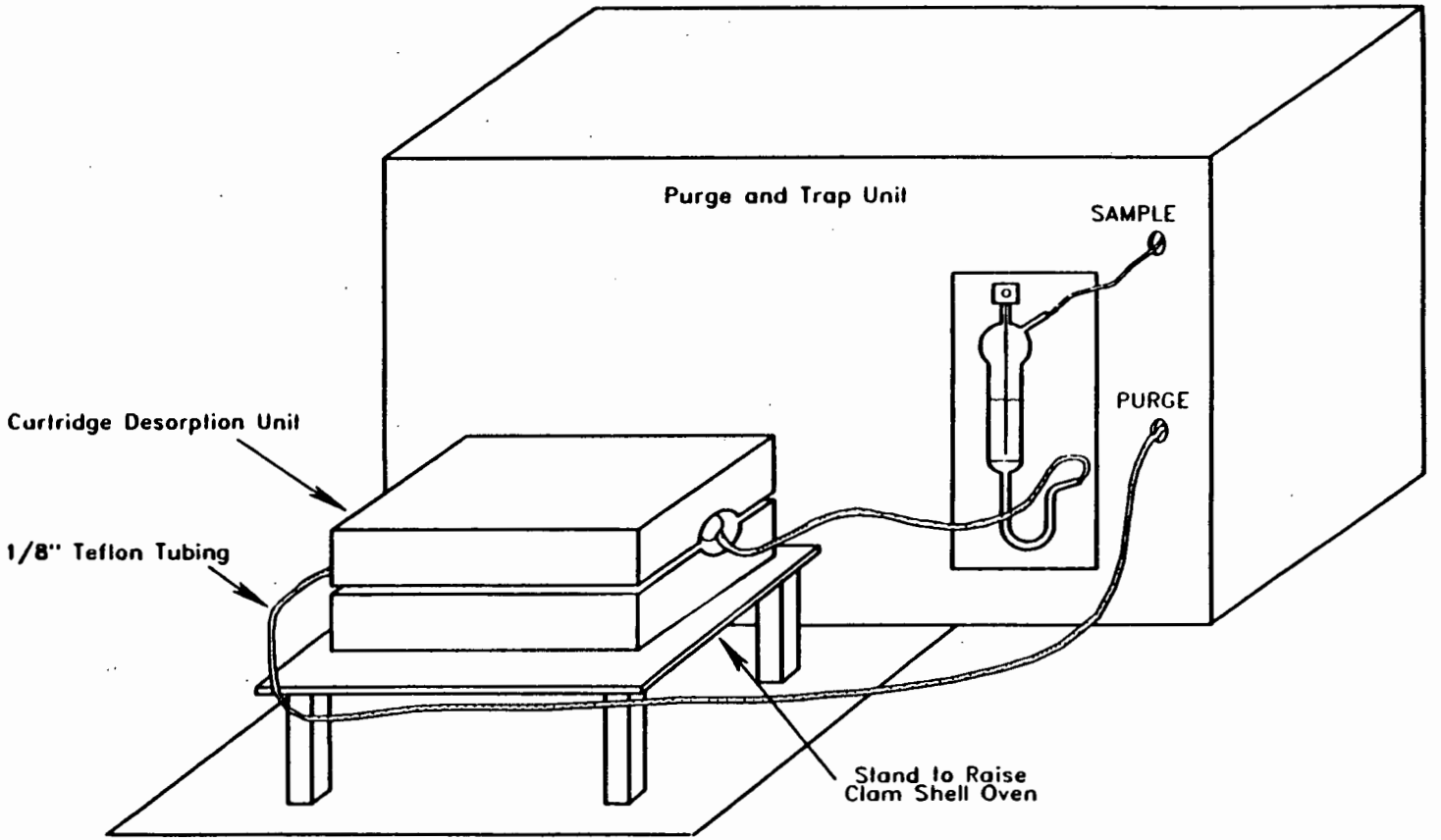


Figure 2. Cartridge Desorption Unit with Purge and Trap Unit

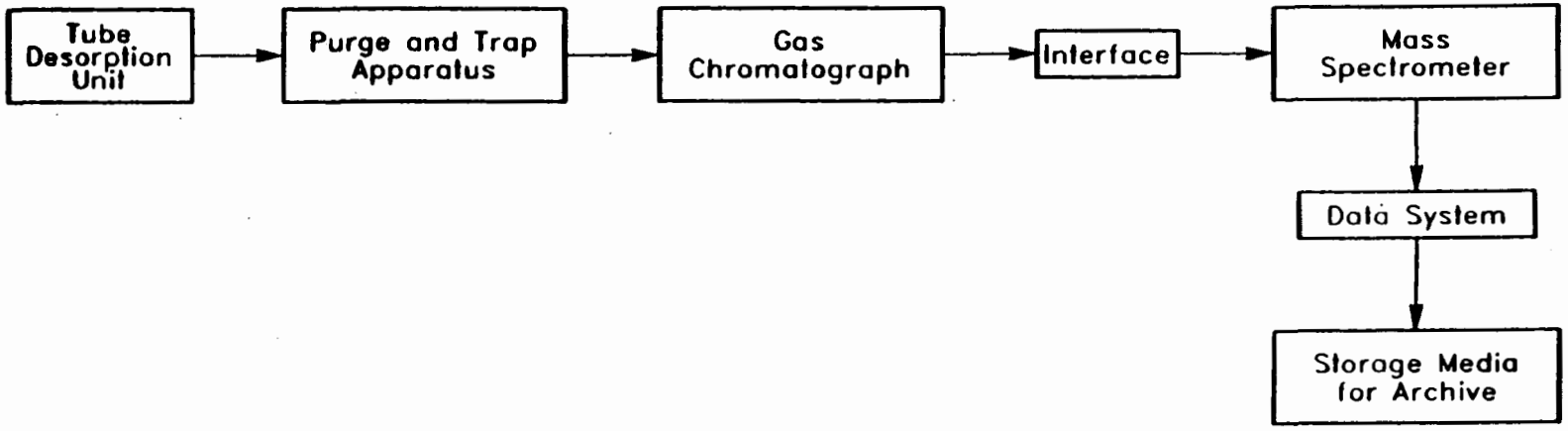


Figure 3. Schematic Diagram of Overall Analytical System

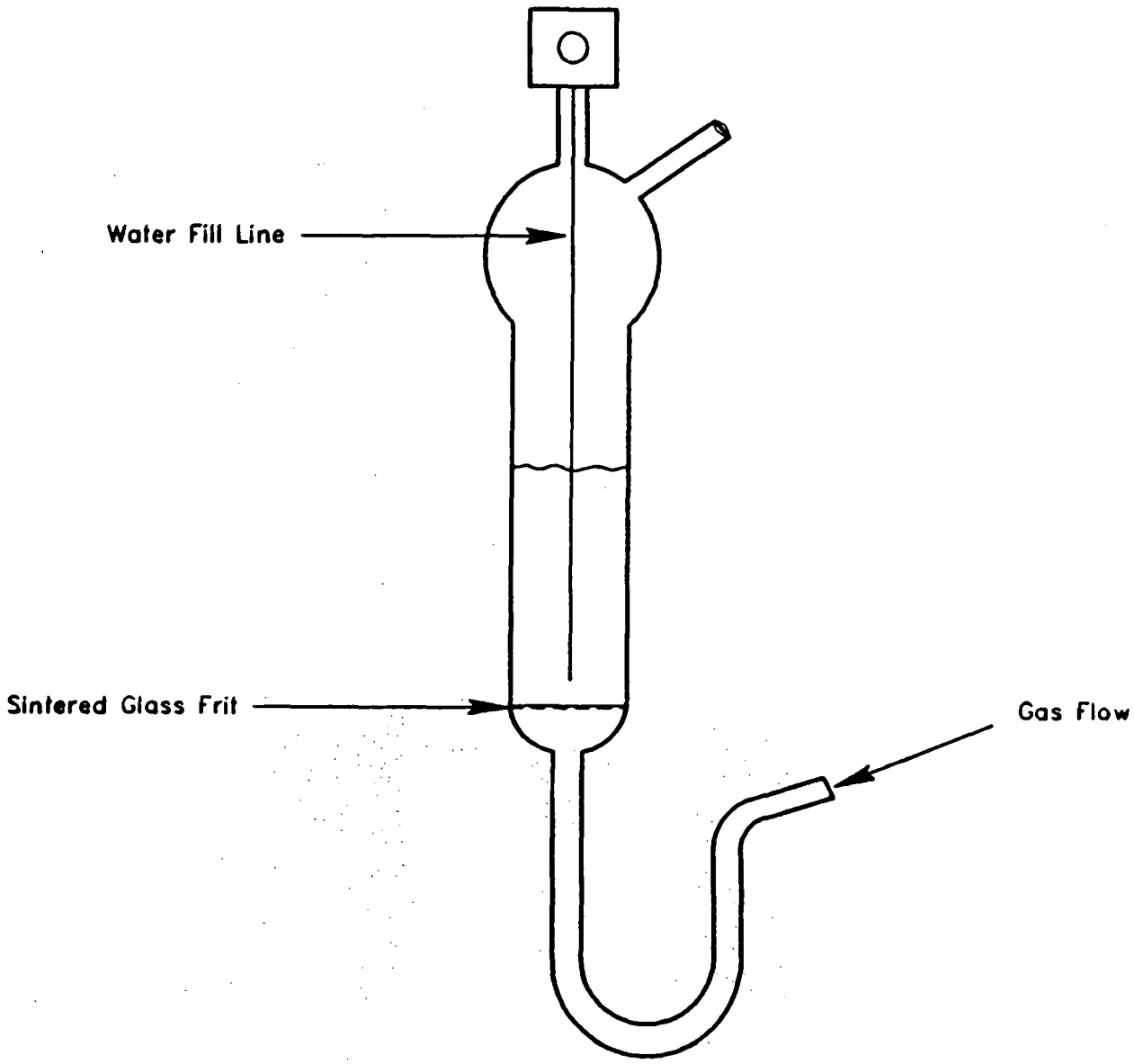


Figure 4. Sample Purge Vessel

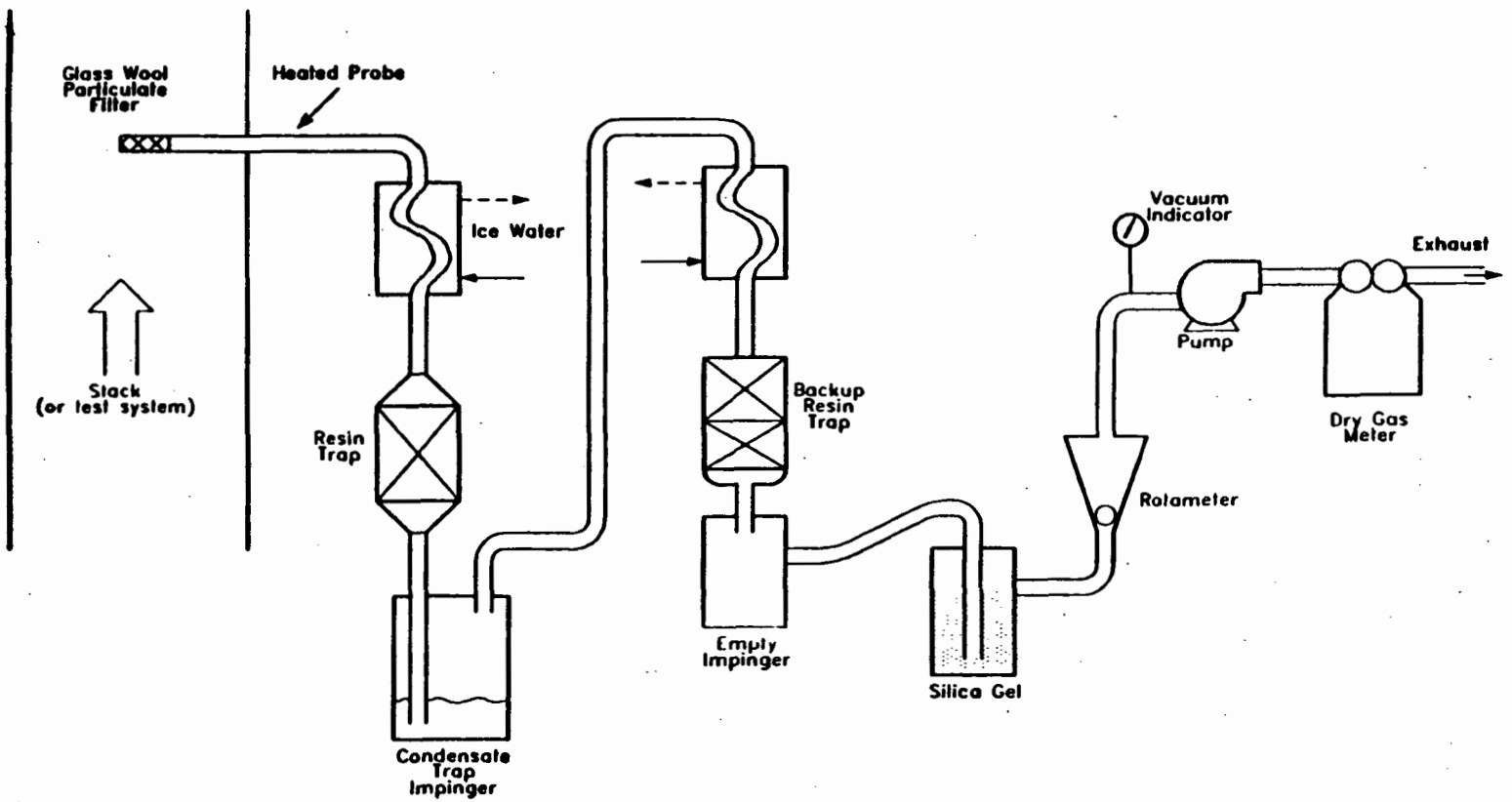
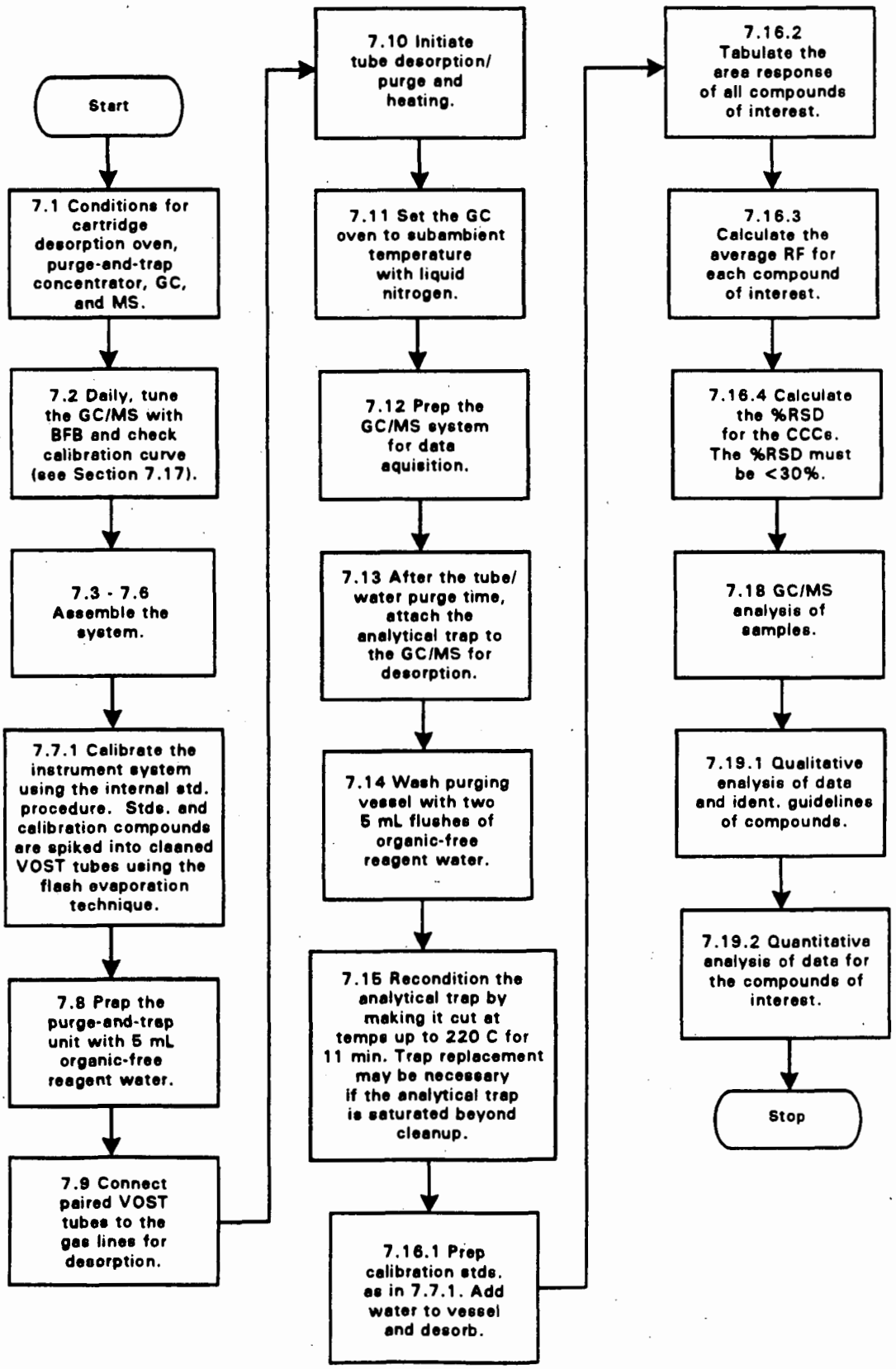


Figure 5. Schematic of Volatile Organic Sampling Train (VOST)


Start
7.1 Conditions for cartridge desorption oven, purge-and-trap concentrator, GC, and MS.
7.2 Daily, tune the GC/MS with BFB and check calibration curve (see Section 7.17).
7.3 - 7.6 Assemble the system.
7.7.1 Calibrate the instrument system using the internal std. procedure. Stds. and calibration compounds are spiked into cleaned VOST tubes using the flash evaporation technique.
7.8 Prep the purge-and-trap unit with 5 mL organic-free reagent water.
7.9 Connect paired VOST tubes to the gas lines for desorption.
7.10 Initiate tube desorption/ purge and heating.
7.11 Set the GC oven to subambient temperature with liquid nitrogen.
7.12 Prep the GC/MS system for data aquisition.
7.13 After the tube/ water purge time, attach the analytical trap to the GC/MS for desorption.
7.14 Wash purging vessel with two 5 mL flushes of organic-free reagent water.
7.15 Recondition the analytical trap by making it cut at temps up to 220 C for 11 min. Trap replacement may be necessary if the analytical trap is saturated beyond cleanup.
7.16.1 Prep calibration stds. as in 7.7.1. Add water to vessel and desorb.
7.16.2 Tabulate the area response of all compounds of interest.
7.16.3 Calculate the average RF for each compound of interest.
7.16.4 Calculate the %RSD for the CCCs. The %RSD must be <30%.
7.18 GC/MS analysis of samples.
7.19.1 Qualitative analysis of data and ident. guidelines of compounds.
7.19.2 Quantitative analysis of data for the compounds of interest.
Stop

METHOD 5050

BOMB PREPARATION METHOD FOR SOLID WASTE

1.0 SCOPE AND APPLICATION

1.1 This method describes the sample preparation steps necessary to determine total chlorine in solid waste and virgin and used oils, fuels and related materials, including: crankcase, hydraulic, diesel, lubricating and fuel oils, and kerosene by bomb oxidation and titration or ion chromatography. Depending on the analytical finish chosen, other halogens (bromine and fluorine) and other elements (sulfur and nitrogen) may also be determined.

1.2 The applicable range of this method varies depending on the analytical finish chosen. In general, levels as low as 500 μg/g chlorine in the original oil sample can be determined. The upper range can be extended to percentage levels by dilution of the combustate.

1.3 This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Specific safety statements are given in Section 3.0.

2.0 SUMMARY OF METHOD

2.1 The sample is oxidized by combustion in a bomb containing oxygen under pressure. The liberated halogen compounds are absorbed in a sodium carbonate/sodium bicarbonate solution. Approximately 30 to 40 minutes are required to prepare a sample by this method. Samples with a high water content (> 25%) may not combust efficiently and may require the addition of a mineral oil to facilitate combustion. Complete combustion is still not guaranteed for such samples.

2.2 The bomb combustate solution can then be analyzed for the following elements as their anion species by one or more of the following methods:

Method	Title
9252	Chloride (Titrimetric, Mercuric Nitrate)
9253	Chloride (Titrimetric, Silver Nitrate)
9056	Inorganic Anions by Ion Chromatography (Chloride, Sulfate, Nitrate, Phosphate, Fluoride, Bromide)

NOTE: Strict adherence to all of the provisions prescribed hereinafter ensures against explosive rupture of the bomb, or a blowout, provided the bomb is of proper design and construction and in good mechanical condition. It is desirable, however, that the bomb be enclosed in a shield of steel plate at least 1/2 in. (12.7 mm) thick, or equivalent protection be provided against unforeseeable contingencies.

3.0 INTERFERENCES

3.1 Samples with very high water content (> 25%) may not combust efficiently and may require the addition of a mineral oil to facilitate combustion.

3.2 To determine total nitrogen in samples, the bombs must first be purged of ambient air. Otherwise, nitrogen results will be biased high.

4.0 APPARATUS AND MATERIALS

4.1 Bomb, having a capacity of not less than 300 mL, so constructed that it will not leak during the test, and that quantitative recovery of the liquids from the bomb may be readily achieved. The inner surface of the bomb may be made of stainless steel or any other material that will not be affected by the combustion process or products. Materials used in the bomb assembly, such as the head gasket and lead-wire insulation, shall be resistant to heat and chemical action and shall not undergo any reaction that will affect the chlorine content of the sample in the bomb.

4.2 Sample cup, platinum or stainless steel, 24 mm in outside diameter at the bottom, 27 mm in outside diameter at the top, 12 mm in height outside, and weighing 10 to 11 g.

4.3 Firing wire, platinum or stainless steel, approximately No. 26 B & S gage.

4.4 Ignition circuit, capable of supplying sufficient current to ignite the nylon thread or cotton wicking without melting the wire.

NOTE: The switch in the ignition circuit shall be of the type that remains open, except when held in closed position by the operator.

4.5 Nylon sewing thread, or Cotton Wicking, white.

4.6 Funnel, to fit a 100-mL volumetric flask.

4.7 Class A volumetric flasks, 100-mL, one per sample.

4.8 Syringe, 5- or 10-mL disposable plastic or glass.

4.9 Apparatus for specific analysis methods are given in the methods.

4.10 Analytical balance: capable of weighing to 0.0001 g.

5.0 REAGENTS

5.1 Purity of reagents. Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Oxygen. Free of combustible material and halogen compounds, available at a pressure of 40 atm.

WARNING: Oxygen vigorously accelerates combustion (see Appendix A1.1)

5.4 Sodium bicarbonate/sodium carbonate solution. Dissolve 2.5200 g $NaHCO_3$ and 2.5440 g Na_2CO_3 in reagent water and dilute to 1 L.

5.5 White oil. Refined.

5.6 Reagents and materials for specific analysis methods are given in the methods.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 Ensure that the portion of the sample used for the test is representative of the sample.

6.3 To minimize losses of volatile halogenated solvents that may be present in the sample, keep the field and laboratory samples as free of headspace as possible.

6.4 Because used oils may contain toxic and/or carcinogenic substances appropriate field and laboratory safety procedures should be followed.

7.0 PROCEDURE

7.1 Sample Preparation

7.1.1 Preparation of bomb and sample. Cut a piece of firing wire approximately 100 mm in length and attach the free ends to the terminals. Arrange the wire so that it will be just above and not touching the sample cup. Loop a cotton thread around the wire so that the ends will extend into the sampling cup. Pipet 10 mL of the $NaHCO_3/Na_2CO_3$ solution into the bomb, wetting the sides. Take an aliquot of the oil sample of approximately 0.5 g using a 5- or 10-mL disposable plastic syringe, and place in the sample cup. The actual sample weight is determined by the difference

between the weight of the empty and filled syringe. Do not use more than 1 g of sample.

NOTE: After repeated use of the bomb for chlorine determination, a film may be noticed on the inner surface. This dullness should be removed by periodic polishing of the bomb. A satisfactory method for doing this is to rotate the bomb in a lathe at about 300 rpm and polish the inside surface with Grit No. 2/0 or equivalent paper[1] coated with a light machine oil to prevent cutting, and then with a paste of grit-free chromic oxide[2] and water. This procedure will remove all but very deep pits and put a high polish on the surface. Before using the bomb, it should be washed with soap and water to remove oil or paste left from the polishing operation. Bombs with porous or pitted surfaces should never be used because of the tendency to retain chlorine from sample to sample.

NOTE: If the sample is not readily combustible, other nonvolatile, chlorine-free combustible diluents such as white oil may be employed. However, the combined weight of sample and nonvolatile diluent shall not exceed 1 g. Some solid additives are relatively insoluble but may be satisfactorily burned when covered with a layer of white oil.

NOTE: The practice of alternately running samples high and low in chlorine content should be avoided whenever possible. It is difficult to rinse the last traces of chlorine from the walls of the bomb, and the tendency for residual chlorine to carry over from sample to sample has been observed in a number of laboratories. When a sample high in chlorine has preceded one low in chlorine content, the test on the low-chlorine sample should be repeated, and one or both of the low values thus obtained should be considered suspect if they do not agree within the limits of repeatability of this method.

NOTE: Do not use more than 1 g total of sample and white oil or other chlorine-free combustible material. Use of excess amounts of these materials could cause a buildup of dangerously high pressure and possible rupture of the bomb.

7.1.2 Addition of oxygen. Place the sample cup in position and arrange the thread so that the end dips into the sample. Assemble the bomb and tighten the cover securely. Admit oxygen slowly (to avoid blowing the oil from the cup) until a pressure is reached as indicated in Table 1.

NOTE: Do not add oxygen or ignite the sample if the bomb has been jarred, dropped, or tiled.

---

[1]Emery Polishing Paper grit No. 2/0 may be purchased from the Behr-Manning Co., Troy, NY.

[2]Chromic oxide may be purchased from J.T. Baker & Co., Phillipsburg, NJ.

7.1.3 Combustion. Immerse the bomb in a cold water bath. Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. Remove the bomb from the bath after immersion for at least 10 minutes. Release the pressure at a slow, uniform rate such that the operation requires at least 1 min. Open the bomb and examine the contents. If traces of unburned oil or sooty deposits are found, discard the determination, and thoroughly clean the bomb before using it again.

7.1.4 Collection of halogen solution. Using reagent water and a funnel, thoroughly rinse the interior of the bomb, the sample cup, the terminals, and the inner surface of the bomb cover into a 100-mL volumetric flask. Dilute to the mark with reagent water.

7.1.5 Cleaning procedure for bomb and sample cup. Remove any residual fuse wire from the terminals and the cup. Using hot water, rinse the interior of the bomb, the sample cup, the terminals, and the inner surface of the bomb cover. (If any residue remains, first scrub the bomb with Alconox solution). Copiously rinse the bomb, cover, and cup with reagent water.

7.2 Sample Analysis. Analyze the combustate for chlorine or other halogens using the methods listed in Step 2.2. It may be necessary to dilute the samples so that the concentration will fall within the range of standards.

7.3 Calculations. Calculate the concentrations of each element detected in the sample according to the following equation:

$$C_o = \frac{C_{com} \times V_{com} \times DF}{W_o} \qquad (1)$$

where:

C_o = concentration of element in the sample, μg/g
C_{com} = concentration of element in the combustate, μg/mL
V_{com} = total volume of combustate, mL
DF = dilution factor
W_o = weight of sample combusted, g.

Report the concentration of each element detected in the sample in micrograms per gram.

Example: A 0.5-g oil sample was combusted, yielding 10 mL of combustate. The combustate was diluted to 100 mL total volume and analyzed for chloride, which was measured to be 5 μg/mL. The concentration of chlorine in the original sample is then calculated as shown below:

$$C_o = \frac{\frac{5\ \mu g}{mL} \times (10\ mL) \times (10)}{0.5\ g} \qquad (2)$$

$$C_o = 1{,}000\ \frac{\mu g}{g} \qquad (3)$$

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 One sample in ten should be bombed twice. The results should agree to within 10%, expressed as the relative percent difference of the results.

8.3 Analyze matrix spike and matrix spike duplicates - spike samples with the elements of interest at a level commensurate with the levels being determined. The spiked compounds should be similar to those expected in the sample. Any sample suspected of containing > 25% water should also be spiked with organic chlorine.

8.4 For higher levels (e.g., percent levels), spiking may be inappropriate. For these cases, samples of known composition should be combusted. The results should agree to within 10% of the expected result.

8.5 Quality control for the analytical method(s) of choice should be followed.

9.0 PERFORMANCE

See analytical methods referenced in Step 2.2.

10.0 REFERENCES

1. ASTM Method D 808-81, Standard Test Method for Chlorine in New and Used Petroleum Products (Bomb Method). 1988 Annual Book of ASTM Standards. Volume 05.01 Petroleum Products and Lubricants.

2. Gaskill, A.; Estes, E. D.; Hardison, D. L.; and Myers, L. E. Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels. Prepared for U.S. Environmental Protection Agency, Office of Solid Waste. EPA Contract No. 68-01-7075, WA 80. July 1988.

TABLE 1.
GAGE PRESSURES

Capacity of bomb, mL	Minimum gage pressure[a], atm	Maximum gage pressure[a], atm
300 to 350	38	40
350 to 400	35	37
400 to 450	30	32
450 to 500	27	29

[a]The minimum pressures are specified to provide sufficient oxygen for complete combustion, and the maximum pressures represent a safety requirement. Refer to manufacturers' specifications for appropriate gage pressure, which may be lower than those listed here.

APPENDIX

A1. PRECAUTIONARY STATEMENTS

A1.1 Oxygen

Warning--Oxygen vigorously accelerates combustion.

Keep oil and grease away. Do not use oil or grease on regulators, gages, or control equipment.

Use only with equipment conditioned for oxygen service by careful cleaning to remove oil, grease, and other combustibles.

Keep combustibles away from oxygen and eliminate ignition sources.

Keep surfaces clean to prevent ignition or explosion, or both, on contact with oxygen.

Always use a pressure regulator. Release regulator tension before opening cylinder valve.

All equipment and containers used must be suitable and recommended for oxygen service.

Never attempt to transfer oxygen from cylinder in which it is received to any other cylinder. Do not mix gases in cylinders.

Do not drop cylinder. Make sure cylinder is secured at all times.

Keep cylinder valve closed when not in use.

Stand away from outlet when opening cylinder valve.

For technical use only. Do not use for inhalation purposes.

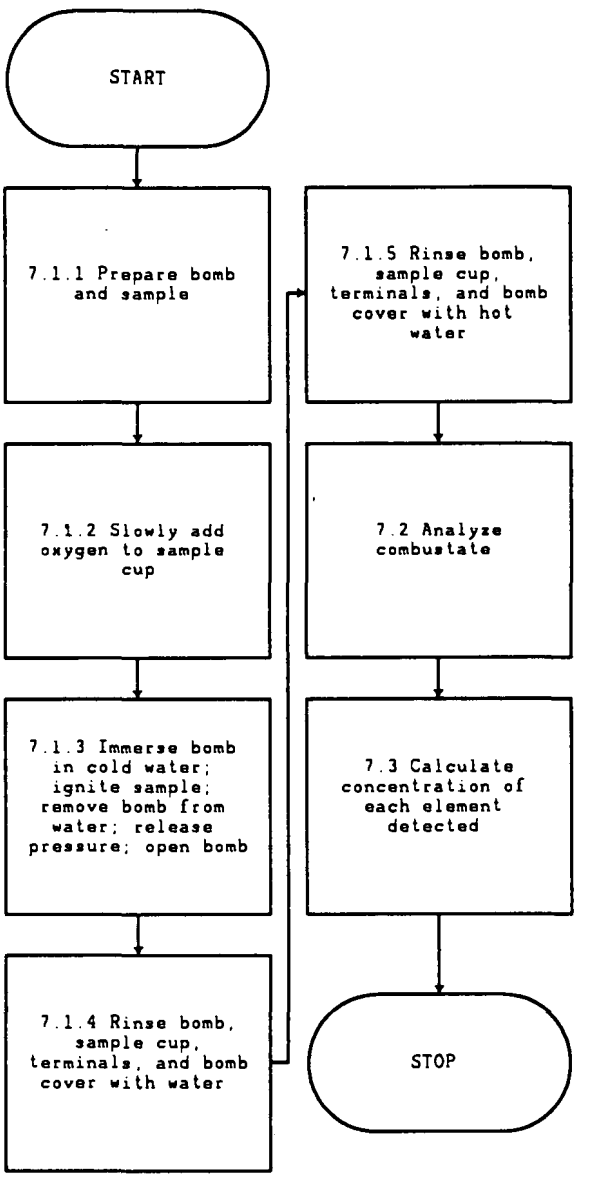
Keep cylinder out of sun and away from heat.

Keep cylinders from corrosive environment.

Do not use cylinder without label.

Do not use dented or damaged cylinders.

See Compressed Gas Association booklets G-4 and G4.1 for details of safe practice in the use of oxygen.


START
7.1.1 Prepare bomb and sample
7.1.2 Slowly add oxygen to sample cup
7.1.3 Immerse bomb in cold water; ignite sample; remove bomb from water; release pressure; open bomb
7.1.4 Rinse bomb, sample cup, terminals, and bomb cover with water
7.1.5 Rinse bomb, sample cup, terminals, and bomb cover with hot water
7.2 Analyze combustate
7.3 Calculate concentration of each element detected
STOP

METHOD 6010A

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-atomic emission spectroscopy (ICP) determines trace elements, including metals, in solution. The method is applicable to all of the elements listed in Table 1. All matrices, including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.

1.2 Elements for which Method 6010 is applicable are listed in Table 1. Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of spectrometer. The data shown in Table 1 provide estimated detection limits for clean aqueous samples using pneumatic nebulization. Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods (e.g. Methods 3005-3050). When analyzing for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 Method 6010 describes the simultaneous, or sequential, multielemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 3.0 should also be recognized and appropriate corrections made; tests for their presence are described in Step 8.5.

TABLE 1.
RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Detection Element	Wavelength[a] (nm)	Estimated Limit[b] (ug/L)
Aluminum	308.215	45
Antimony	206.833	32
Arsenic	193.696	53
Barium	455.403	2
Beryllium	313.042	0.3
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Lithium	670.784	5
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Phosphorus	213.618	51
Potassium	766.491	See note c
Selenium	196.026	75
Silver	328.068	7
Sodium	588.995	29
Strontium	407.771	0.3
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

[a]The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Step 3.1). In time, other elements may be added as more information becomes available and as required.

[b]The estimated instrumental detection limits shown are taken from Reference 1 in Section 10.0 below. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

[c]Highly dependent on operating conditions and plasma position.

3.0 INTERFERENCES

3.1 Spectral interferences are caused by: (1) overlap of a spectral line from another element at the analytical or background measurement wavelengths; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuum or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of all ICP instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Recommended wavelengths are listed in Table 1 and potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed.

3.1.1 Element-specific interference is expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately 0.13 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, argon flow rate, etc. The user should be aware of the possibility of interferences other than those specified in Table 2 and that analysts should be aware of these interferences when conducting analyses.

3.1.2 The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferent concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

3.1.3 At present, information on the listed silver and potassium wavelengths is not available, but it has been reported that second-order energy from the magnesium 383.231-nm wavelength interferes with the listed potassium line at 766.491 nm.

TABLE 2.

ANALYTE CONCENTRATION EQUIVALENTS ARISING FROM INTERFERENCE AT THE 100-mg/L LEVEL

		Interferent[a,b]									
Analyte	Wavelength (nm)	Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Tl	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

[a]Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

Al - 1000 mg/L
Ca - 1000 mg/L
Cr - 200 mg/L
Cu - 200 mg/L
Fe - 1000 mg/L
Mg - 1000 mg/L
Mn - 200 mg/L
Tl - 200 mg/L
V - 200 mg/L

[b]The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferent figure.

3.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. Differences in solution volatility can also cause inaccuracies when organic solvents are involved. If physical interferences are present, they must be reduced by diluting the sample or by using a peristaltic pump. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Changing the nebulizer and removing salt buildup at the tip of the torch sample injector can be used as an additional measure to control salt buildup. Also, it has been reported that better control of the argon flow rate improves instrument performance; this is accomplished with the use of mass flow controllers.

3.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled argon plasma emission spectrometer:

4.1.1 Computer-controlled emission spectrometer with background correction.

4.1.2 Radio frequency generator compliant with FCC regulations.

4.1.3 Argon gas supply - Welding grade or better.

4.2 Operating conditions - The analyst should follow the instructions provided by the instrument manufacturer. For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within the instrument linear range where spectral interference correction factors are valid. The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

4.3 Class A volumetric flasks

4.4 Class A volumetric pipets

4.5 Analytical balance - capable of accurate measurement to 4 significant figures.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question analyze for contamination. If the concentration is less than the MDL then the reagent is acceptable.

5.1.1 Hydrochloric acid (conc), HCl.

5.1.2 Hydrochloric acid (1:1), HCl. Add 500 mL concentrated HCl to 400 mL water and dilute to 1 liter in an appropriate beaker.

5.1.3 Nitric acid (conc), HNO_3.

5.1.4 Nitric acid (1:1), HNO_3. Add 500 mL concentrated HNO_3 to 400 mL water and dilute to 1 liter in an appropriate beaker.

5.2 Reagent Water. All references to water in the method refer to reagent water unless otherwise specified. Reagent water will be interference free. Refer to Chapter One for a definition of reagent water.

5.3 Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hour at 105°C, unless otherwise specified.

<u>CAUTION</u>: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure metal added, or with the use of the mole fraction and the weight of the metal salt added.

Metal

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

Metal salts

$$\text{Concentration (ppm)} = \frac{\text{weight (mg) x mole fraction}}{\text{volume (L)}}$$

5.3.1 Aluminum solution, stock, 1 mL = 1000 ug Al: Dissolve 1.0 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4 mL of (1:1) HCl and 1 mL of concentrated HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional

10 mL of (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.2 Antimony solution, stock, 1 mL = 1000 ug Sb: Dissolve 2.70 g $K(SbO)C_4H_4O_6$ (mole fraction Sb = 0.3749), weighed accurately to at least four significant figures, in water, add 10 mL (1:1) HCl, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.3 Arsenic solution, stock, 1 mL = 1000 ug As: Dissolve 1.30 g of As_2O_3 (mole fraction As = 0.7574), weighed accurately to at least four significant figures, in 100 mL of water containing 0.4 g NaOH. Acidify the solution with 2 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water

5.3.4 Barium solution, stock, 1 mL = 1000 ug Ba: Dissolve 1.50 g $BaCl_2$ (mole fraction Ba = 0.6595), dried at 250°C for 2 hours, weighed accurately to at least four significant figures, in 10 mL water with 1 mL (1:1) HCl. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.5 Beryllium solution, stock, 1 mL = 1000 ug Be: Do not dry. Dissolve 19.7 g $BeSO_4 \cdot 4H_2O$ (mole fraction Be = 0.0509), weighed accurately to at least four significant figures, in water, add 10.0 mL concentrated HNO_3, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.6 Cadmium solution, stock, 1 mL = 1000 ug Cd: Dissolve 1.10 g CdO (mole fraction Cd = 0.8754), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.7 Calcium solution, stock, 1 mL = 1000 ug Ca: Suspend 2.50 g $CaCO_3$ (mole Ca fraction = 0.4005), dried at 180°C for 1 hour before weighing, weighed accurately to at least four significant figures, in water and dissolve cautiously with a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.8 Chromium solution, stock, 1 mL = 1000 ug Cr: Dissolve 1.90 g CrO_3 (mole fraction Cr = 0.5200), weighed accurately to at least four significant figures, in water. When solution is complete, acidify with 10 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.9 Cobalt solution, stock, 1 mL = 1000 ug Co: Dissolve 1.00 g of cobalt metal, weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.10 Copper solution, stock, 1 mL = 1000 ug Cu: Dissolve 1.30 g CuO (mole fraction Cu = 0.7989), weighed accurately to at least four significant figures), in a minimum amount of (1:1) HNO_3. Add 10.0 mL

concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.11 Iron solution, stock, 1 mL = 1000 ug Fe: Dissolve 1.40 g Fe_2O_3 (mole fraction Fe = 0.6994), weighed accurately to at least four significant figures, in a warm mixture of 20 mL (1:1) HCl and 2 mL of concentrated HNO_3. Cool, add an additional 5.0 mL of concentrated HNO_3, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.12 Lead solution, stock, 1 mL = 1000 ug Pb: Dissolve 1.60 g $Pb(NO_3)_2$ (mole fraction Pb = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10 mL (1:1) HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.13 Lithium solution, stock, 1 mL = 1000 ug Li: Dissolve 5.324 g lithium carbonate (mole fraction Li = 0.1878), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.14 Magnesium solution, stock, 1 mL = 1000 ug Mg: Dissolve 1.70 g MgO (mole fraction Mg = 0.6030), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.15 Manganese solution, stock, 1 mL = 1000 ug Mn: Dissolve 1.00 g of manganese metal, weighed accurately to at least four significant figures, in acid mixture (10 mL concentrated HCl and 1 mL concentrated HNO_3) and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.16 Molybdenum solution, stock, 1 mL = 1000 ug Mo: Dissolve 2.00 g $(NH_4)_6Mo_7O_{24}.4H_2O$ (mole fraction Mo = 0.5772), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.17 Nickel solution, stock, 1 mL = 1000 ug Ni: Dissolve 1.00 g of nickel metal, weighed accurately to at least four significant figures, in 10.0 mL hot concentrated HNO_3, cool, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.18 Phosphate solution, stock, 1 mL = 1000 ug P: Dissolve 4.393 g anhydrous KH_2PO_4 (mole fraction P = 0.2276), weighed accurately to at least four significant figures, in water. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.19 Potassium solution, stock, 1 mL = 1000 ug K: Dissolve 1.90 g KCl (mole fraction K = 0.5244) dried at 110°C, weighed accurately to at least four significant figures, in water, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.20 Selenium solution, stock, 1 mL = 1000 ug Se: Do not dry. Dissolve 1.70 g H_2SeO_3 (mole fraction Se = 0.6123), weighed accurately to

at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.21 Silver solution, stock, 1 mL = 1000 ug Ag: Dissolve 1.60 g $AgNO_3$ (mole fraction Ag = 0.6350), weighed accurately to at least four significant figures, in water and 10 mL concentrated HNO_3. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.22 Sodium solution, stock, 1 mL = 1000 ug Na: Dissolve 2.50 g NaCl (mole fraction Na = 0.3934), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.23 Strontium solution, stock, 1 mL = 1000 ug Sr: Dissolve 2.415 g of strontium nitrate ($Sr(NO_3)_2$) (mole fraction 0.4140), weighed accurately to at least four significant figures, in a 1-liter flask containing 10 mL of concentrated HCl and 700 mL of water. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.24 Thallium solution, stock, 1 mL = 1000 ug Tl: Dissolve 1.30 g $TlNO_3$ (mole fraction Tl = 0.7672), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.25 Vanadium solution, stock, 1 mL = 1000 ug V: Dissolve 2.30 g NH_4O_3 (mole fraction V = 0.4356), weighed accurately to at least four significant figures, in a minimum amount of concentrated HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.26 Zinc solution, stock, 1 mL = 1000 ug Zn: Dissolve 1.20 g ZnO (mole fraction Zn = 0.8034), weighed accurately to at least four significant figures, in a minimum amount of dilute HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.4 Mixed calibration standard solutions - Prepare mixed calibration tandard solutions by combining appropriate volumes of the stock solutions in olumetric flasks (see Table 3). Matrix match with the appropriate acids and ilute to 100 mL with water. Prior to preparing the mixed standards, each stock olution should be analyzed separately to determine possible spectral nterference or the presence of impurities. Care should be taken when preparing he mixed standards to ensure that the elements are compatible and stable ogether. Transfer the mixed standard solutions to FEP fluorocarbon or previously nused polyethylene or polypropylene bottles for storage. Fresh mixed standards hould be prepared, as needed, with the realization that concentration can change n aging. Calibration standards must be initially verified using a quality ontrol sample (see Step 5.8) and monitored weekly for stability. Some typical alibration standard combinations are listed in Table 3. All mixtures should then e scanned using a sequential spectrometer to verify the absence of interelement pectral interference in the recommended mixed standard solutions.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

TABLE 3.
MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo
IV	Al, Ca, Cr, K, Na, Ni,Li,& Sr
V	Ag (see Note to Step 5.4), Mg, Sb, and Tl
VI	P

5.5 Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

5.5.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. Prepare a sufficient quantity to flush the system between standards and samples.

5.5.2 The method blank must contain all the reagents and in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

5.6 The instrument check standard is prepared by the analyst by combining compatible elements at concentrations equivalent to the midpoint of their respective calibration curves (see Step 8.6.1.1 for use). The instrument check standard should be prepared from a source independent from that used in the calibration standards.

5.7 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate

5.7 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the instrumental detection limits. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

5.8 The quality control sample should be prepared in the same acid matrix as the calibration standards at 10 times the instrumental detection limits and in accordance with the instructions provided by the supplier.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the material in Chapter Three, Metallic Analytes, Steps 3.1 through 3.3.

7.0 PROCEDURE

7.1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Water samples which have been prefiltered and acidified will not need acid digestion as long as the samples and standards are matrix matched. Solubilization and digestion procedures are presented in Sample Preparation Methods (Methods 3005A-3050A).

7.2 Set up the instrument with proper operating parameters established in Step 4.2. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration).

7.3 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Step 5.4. Flush the system with the calibration blank (Step 5.5.1) between each standard or as the manufacturer recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve should consist of a blank and three standards.

7.4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

7.5 Flush the system with the calibration blank solution for at least 1 minute (Step 5.5.1) before the analysis of each sample (see Note to Step 7.3). Analyze the instrument check standard (Step 5.6) and the calibration blank (Step 5.5.1) after each 10 samples.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection. Refer to Chapter One for additional quality control procedures.

8.2 Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.

8.3 Employ a minimum of one method blank per sample batch to determine if contamination or any memory effects are occurring. A method blank is a volume of reagent water acidified with the same amounts of acids as were the standards and samples.

8.4 Analyze one replicate sample for every twenty samples or per analytical batch, whichever is more frequent. A replicate sample is a sample brought through the whole sample preparation and analytical process in duplicate. Refer to Chapter One for a more detailed description of an analytical batch.

8.5 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in Steps 8.5.1 and 8.5.2, will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

8.5.1 Serial dilution: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:4 dilution should agree within ± 10% of the original determination. If not, a chemical or physical interference effect should be suspected.

8.5.2 Post digestion spike addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected.

<u>CAUTION</u>: If spectral overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

8.6 Check the instrument standardization by analyzing appropriate check standards as follows.

8.6.1 Verify calibration every 10 samples and at the end of the analytical run, using a calibration blank (Step 5.5.1) and a check standard (Step 5.6).

8.6.1.1 The results of the check standard are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and reanalyze the previous ten samples.

8.6.1.2 The results of the calibration blank are to agree within three standard deviations of the mean blank value. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples.

8.6.2 Verify the interelement and background correction factors at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Do this by analyzing the interference check solution (Step 5.7). Results should be within ± 20% of the true value obtained in Step 8.6.1.1.

8.6.3 Spiked replicate samples are to be analyzed at a frequency of 5% or per analytical batch, whichever is more frequent.

8.6.3.1 The relative percent difference between replicate determinations is to be calculated as follows:

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100$$

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (replicate).

(A control limit of ± 20% RPD shall be used for sample values greater than ten times the instrument detection limit.)

8.6.3.2 The spiked replicate sample recovery is to be within ± 20% of the actual value.

9.0 METHOD PERFORMANCE

9.1 In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

9.2 In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was 9 ± 2%. The mean percent recovery of spiked elements for all wastes was 93 ± 6%. Spike levels ranged from 100 ug/L to 100 mg/L. The wastes included sludges and industrial wastewaters.

10.0 REFERENCES

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3. Patel, B.K.; Raab, G.A.; et al. Report on a Single Laboratory Evaluation of Inductively Coupled Optical Emission Method 6010; EPA Contract No. 68-03-3050, December 1984.

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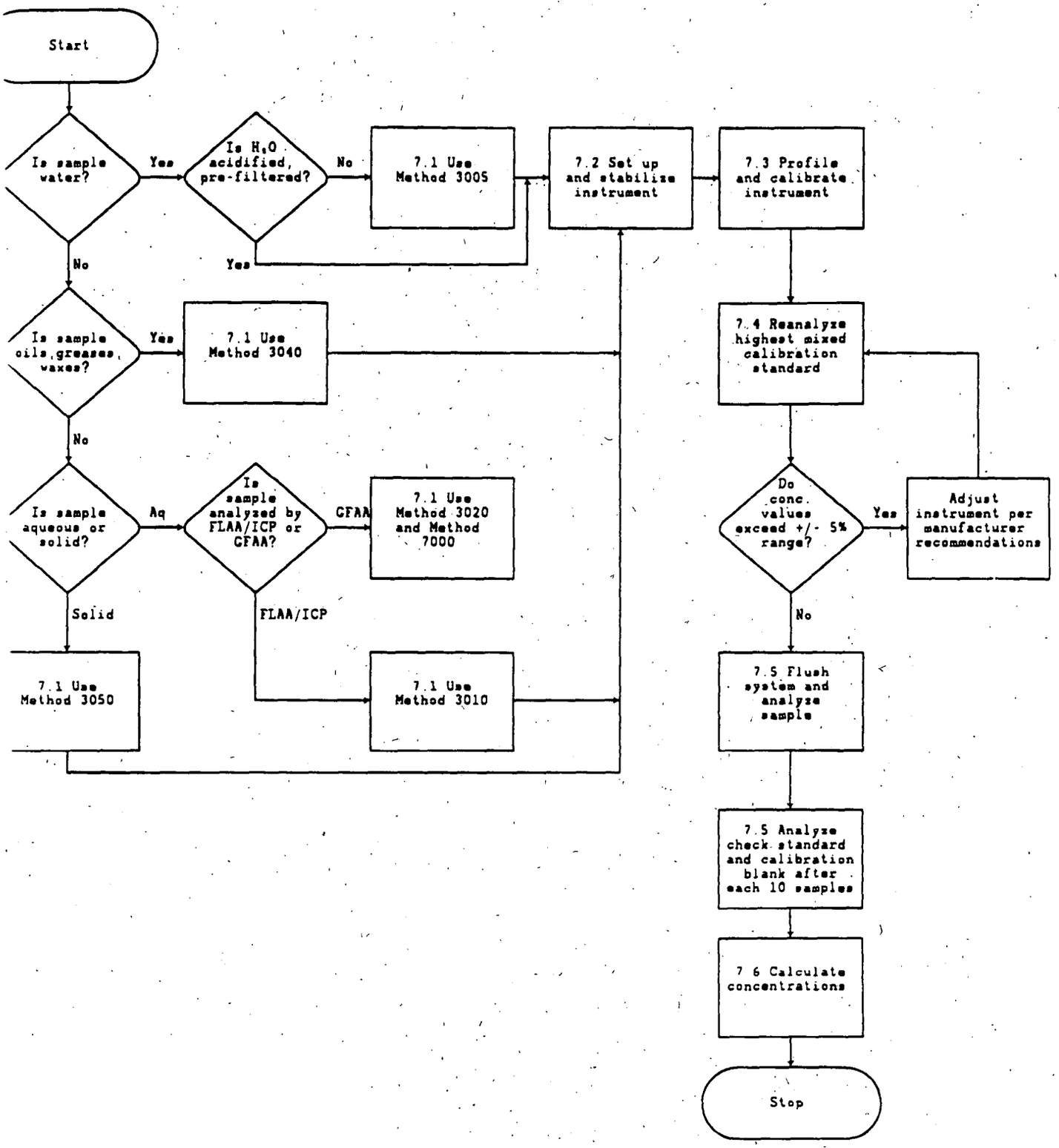
TABLE 4.
ICP PRECISION AND ACCURACY DATA[a]

Element	Sample No. 1 True Value (ug/L)	Sample No. 1 Mean Reported Value (ug/L)	Sample No. 1 Mean SD[b] (%)	Sample No. 2 True Value (ug/L)	Sample No. 2 Mean Reported Value (ug/L)	Sample No. 2 Mean SD[b] (%)	Sample No. 3 True Value (ug/L)	Sample No. 3 Mean Reported Value (ug/L)	Sample No. 3 Mean SD[b] (%)
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	12	2.5	2.9	16	14	13	16
Co	700	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se[c]	40	32	21.9	6	8.5	42	10	8.5	8.3

[a]Not all elements were analyzed by all laboratories.

[b]SD = standard deviation.

[c]Results for Se are from two laboratories.


Start
Is sample water?
Yes
Is H_2O acidified, pre-filtered?
No
7.1 Use Method 3005
Yes
No
Is sample oils, greases, waxes?
Yes
7.1 Use Method 3040
No
Is sample aqueous or solid?
Aq
Is sample analyzed by FLAA/ICP or GFAA?
GFAA
7.1 Use Method 3020 and Method 7000
Solid
FLAA/ICP
7.1 Use Method 3050
7.1 Use Method 3010
7.2 Set up and stabilize instrument
7.3 Profile and calibrate instrument
7.4 Reanalyze highest mixed calibration standard
Do conc. values exceed +/- 5% range?
Yes
Adjust instrument per manufacturer recommendations
No
7.5 Flush system and analyze sample
7.5 Analyze check standard and calibration blank after each 10 samples
7 6 Calculate concentrations
Stop

METHOD 6020

INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of sub-μg/L concentrations of a large number of elements in water samples and in waste extracts or digests [1,2]. When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are required.

1.2 ICP-MS has been applied to the determination of over 60 elements in various matrices. Analytes for which EPA has demonstrated the acceptability of Method 6020 in a multi-laboratory study on solid wastes are listed in Table 1. Acceptability of the method for an element was based upon the multi-laboratory performance compared with that of either furnace atomic absorption spectroscopy or inductively coupled plasma-atomic emission spectroscopy. It should be noted that the multi-laboratory study was conducted in 1986. Multi-laboratory performance data for the listed elements (and others) are provided in Section 9. Instrument detection limits, sensitivities, and linear ranges will vary with the matrices, instrumentation, and operating conditions. In relatively simple matrices, detection limits will generally be below 0.02 μg/L.

1.3 If Method 6020 is used to determine any analyte not listed in Table 1, it is the responsibility of the analyst to demonstrate the accuracy and precision of the Method in the waste to be analyzed. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality (see Section 8.4).

1.4 Use of this method is restricted to spectroscopists who are knowledgeable in the recognition and in the correction of spectral, chemical, and physical interferences in ICP-MS.

1.5 An appropriate internal standard is required for each analyte determined by ICP-MS. Recommended internal standards are ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho, and ^{209}Bi. The lithium internal standard should have an enriched abundance of ^{6}Li, so that interference from lithium native to the sample is minimized. Other elements may need to be used as internal standards when samples contain significant amounts of the recommended internal standards.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples which require total ("acid-leachable") values must be digested using appropriate sample preparation methods (such as Methods 3005 - 3051).

2.2 Method 6020 describes the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

3.0 INTERFERENCES

3.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or analysis using another verified and documented isoptope, or use of another method.

3.2 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature [3,4]. Examples include $ArCl^+$ ions on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. While the <u>approach</u> used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundances from the literature [5], the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals <u>observed</u> for a standard solution at a concentration providing suitable (<1 percent) counting statistics. Because the ^{35}Cl natural abundance of 75.77 percent is 3.13 times the ^{37}Cl abundance of 24.23 percent, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^+$ contribution at m/z 75 is a negligible 0.06 percent of the $^{40}Ar^{35}Cl^+$ signal):

> corrected arsenic signal (using natural isotopes abundances for coefficient approximations) =
>
> (m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal),
> (where the final term adjusts for any selenium contribution at 77 m/z),
>
> <u>NOTE</u>: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}Se^+$, (e.g., $^{81}BrH^+$ from bromine wastes [6]).

Similarly,

corrected cadmium signal (using natural isotopes abundances for coefficient approximations) =

(m/z 114 signal) - (0.027)(m/z 118 signal) - (1.63)(m/z 108 signal), (where last 2 terms adjust for any tin or MoO^+ contributions at m/z 114).

NOTE: Cadmium values will be biased low by this type of equation when $^{92}ZrO^+$ ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct ($^{94}ZrOH^+$) and indirect ($^{90}ZrO^+$) additive interferences when Zr is present.

NOTE: As for the arsenic equation above, the coefficients in the Cd equation are **ONLY** illustrative. The most appropriate coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting precision.

The accuracy of these types of equations is based upon the constancy of the OBSERVED isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found [7] to be reliable, e.g., oxide levels can vary. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferant. This type of correction has been reported [7] for oxide-ion corrections using ThO^+/Th^+ for the determination of rare earth elements. The use of aerosol desolvation and/or mixed plasmas have been shown to greatly reduce molecular interferences [8]. These techniques can be used provided that method detection limits, accuracy, and precision requirements for analysis of the samples can be met.

3.3 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement [9]. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) have been currently recommended [10] to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes [11]. When the intensity level of an internal standard is less than 30 percent or greater than 120 percent of the intensity of the first standard used during calibration, the sample must be reanalyzed after a fivefold (1+4) or greater dilution has been performed.

3.4 Memory interferences can occur when there are large concentration differences between samples or standards which are analyzed sequentially. Sample

deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences which are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled plasma-mass spectrometer:

4.1.1 A system capable of providing resolution, better than or equal to amu at 10% peak height is required. The system must have a mass range from at least 6 to 240 amu and a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass-flow controller for the nebulizer argon and a peristaltic pump for the sample solution are recommended.

4.1.2 Argon gas supply: high-purity grade (99.99%).

5.0 REAGENTS

5.1 Acids used in the preparation of standards and for sample processing must be of high purity. Redistilled acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at less than 2 per cent (v/v) is required for ICP-MS to minimize damage to the interface and to minimize isobaric molecular-ion interferences with the analytes. Many more molecular-ion interferences are observed on the analytes when hydrochloric and sulfuric acids are used [3,4]. Concentrations of antimony and silver between 50-500 µg/L require 1% (v/v) HCl for stability; for concentrations above 500 µg/L Ag, additional HCl will be needed.

5.2 Reagent water: All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99 or greater purity). See Method 6010A, Section 5.3, for instructions on preparing standard solutions from solids.

5.3.1 Bismuth internal standard solution, stock, 1 mL = 100 µg Bi: Dissolve 0.1115 g Bi_2O_3 in a minimum amount of dilute HNO_3. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.2 Holmium internal standard solution, stock, 1 mL = 100 µg Ho: Dissolve 0.1757 g $Ho_2(CO_3)_2 \cdot 5H_2O$ in 10 mL reagent water and 10 mL HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.3 Indium internal standard solution, stock, 1 mL = 100 µg In: Dissolve 0.1000 g indium metal in 10 mL conc. HNO_3. Dilute to 1,000 mL with reagent water.

5.3.4 Lithium internal standard solution, stock, 1 mL = 100 μg ^{6}Li: Dissolve 0.6312 g 95-atom-% ^{6}Li, Li_2CO_3 in 10 mL of reagent water and 10 mL HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.5 Rhodium internal standard solution, stock, 1 mL = 100 μg Rh: Dissolve 0.3593 g ammonium hexachlororhodate (III) $(NH_4)_3RhCl_6$ in 10 mL reagent water. Add 100 mL conc. HCl and dilute to 1,000 mL with reagent water.

5.3.6 Scandium internal standard solution, stock, 1 mL = 100 μg Sc: Dissolve 0.15343 g Sc_2O_3 in 10 mL (1+1) hot HNO_3. Add 5 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.7 Terbium internal standard solution, stock, 1 mL = 100 μg Tb: Dissolve 0.1828 g $Tb_2(CO_3)_3 \cdot 5H_2O$ in 10 mL (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Add 5 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.8 Yttrium internal standard solution, stock, 1 mL = 100 μg Y: Dissolve 0.2316 g $Y_2(CO_3)_3.3H_2O$ in 10 mL (1+1) HNO_3. Add 5 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.9 Titanium solution, stock, 1 mL = 100 μg Ti: Dissolve 0.4133 g $(NH_4)_2TiF_6$ in reagent water. Add 2 drops conc. HF and dilute to 1,000 mL with reagent water.

5.3.10 Molybdenum solution, stock, 1 mL = 100 μg Mo: Dissolve 0.2043 g $(NH_4)_2MoO_4$ in reagent water. Dilute to 1,000 mL with reagent water.

5.4 Mixed calibration standard solutions are prepared by diluting the stock-standard solutions to levels in the linear range for the instrument in a solvent consisting of 1 percent (v/v) HNO_3 in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. Internal standards may be added on-line at the time of analysis using a second channel of the peristaltic pump and an appropriate mixing manifold.) Generally, an internal standard should be no more than 50 amu removed from the analyte. Recommended internal standards include ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{169}Ho, and ^{209}Bi. Prior to preparing the mixed standards, each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Care must be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to freshly acid-cleaned FEP fluorocarbon bottles for storage. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging. Calibration standards must be initially verified using a quality control standard (see Section 5.7) and monitored weekly for stability.

5.5 Blanks: Three types of blanks are required for the analysis. The calibration blank is used in establishing the calibration curve. The preparation blank is used to monitor for possible contamination resulting from the sample preparation procedure. The rinse blank is used to flush the system between all samples and standards.

5.5.1 The calibration blank consists of the same concentration(s) of the same acid(s) used to prepare the final dilution of the calibrating solutions of the analytes [often 1 percent HNO_3 (v/v) in reagent water] along with the selected concentrations of internal standards such that there is an appropriate internal standard element for each of the analytes. Use of HCl for antimony and silver is cited in Section 5.1

5.5.2 The preparation (or reagent) blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the sample solutions.

5.5.3 The rinse blank consists of 1 to 2 percent HNO_3 (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples.

NOTE: The ICS solutions in Table 2 are intended to evaluate corrections for known interferences on only the analytes in Table 1. If Method 6020 is used to determine an element not listed in Table 1, it is the responsibility of the analyst to modify the ICS solutions, or prepare an alternative ICS solution, to allow adequate verification of correction of interferences on the unlisted element (see section 8.4).

5.6 The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl^{16}O^+$ on $^{51}V^+$ and $^{40}Ar^{35}Cl^+$ on $^{75}As^+$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

5.6.1 These solutions must be prepared from ultra-pure reagents. They can be obtained commercially or prepared by the following procedure.

5.6.1.1 Mixed ICS solution I may be prepared by adding 13.903 g $Al(NO_3)_3 \cdot 9H_2O$, 2.498 g $CaCO_3$ (dried at 180 C for 1 h before weighing), 1.000 g Fe, 1.658 g MgO, 2.305 g Na_2CO_3, and 1.767 g K_2CO_3 to 25 mL of reagent water. Slowly add 40 mL of (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Cool and dilute to 1,000 mL with reagent water.

5.6.1.2 Mixed ICS solution II may be prepared by slowly adding 7.444 g 85 % H_3PO_4, 6.373 g 96% H_2SO_4, 40.024 g 37% HCl, and 10.664 g citric acid $C_6O_7H_8$ to 100 mL of reagent water. Dilute to 1,000 mL with reagent water.

5.6.1.3 Mixed ICS solution III may be prepared by adding 1.00 mL each of 100-µg/mL arsenic, cadmium, chromium, cobalt, copper, manganese, nickel, silver, and zinc stock solutions to about 50 mL reagent water. Add 2.0 mL concentrated HNO_3, and dilute to 100.0 mL with reagent water.

5.6.1.4 Working ICS Solutions

5.6.1.4.1 ICS-A may be prepared by adding 10.0 mL of mixed ICS solution I (5.7.1.1), 2.0 mL each of 100-µg/mL titanium stock solution (5.3.9) and molybdenum stock solution (5.3.10), and 5.0 mL of mixed ICS solution II (5.7.1.2). Dilute to 100 mL with reagent water. ICS solution A must be prepared fresh weekly.

5.6.1.4.2 ICS-AB may be prepared by adding 10.0 mL of mixed ICS solution I (5.7.1.1), 2.0 mL each of 100-µg/mL titanium stock solution (5.3.9) and molybdenum stock solution (5.3.10), 5.0 mL of mixed ICS solution II (5.7.1.2), and 2.0 mL of Mixed ICS solution III (5.7.1.3). Dilute to 100 mL with reagent water. Although the ICS solution AB must be prepared fresh weekly, the analyst should be aware that the solution may precipitate silver more quickly.

5.7 The quality control standard is the initial calibration verification solution (ICV), which must be prepared in the same acid matrix as the calibration standards. This solution must be an independent standard near the midpoint of the linear range at a concentration other than that used for instrument calibration. An independent standard is defined as a standard composed of the analytes from a source different from those used in the standards for instrument calibration.

5.8 Mass spectrometer tuning solution. A solution containing elements representing all of the mass regions of interest (for example, 10 µg/L of Li, Co, In, and Tl) must be prepared to verify that the resolution and mass calibration of the instrument are within the required specifications (see Section 7.5). This solution is also used to verify that the instrument has reached thermal stability (See Section 7.4).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Sample collection procedures should address the considerations described in Chapter Nine of this Manual.

6.2 See the introductory material in Chapter Three, Inorganic Analytes, Sections 3.1.3 for information on sample handling and preservation. Only polyethylene or fluorocarbon (TFE or PFA) containers are recommended for use in Method 6020.

7.0 PROCEDURE

7.1 Solubilization and digestion procedures are presented in the Sample Preparation Methods (e.g., Methods 3005 - 3051).

7.2 Initiate appropriate operating configuration of the instruments computer according to the instrument manufacturer's instructions.

7.3 Set up the instrument with the proper operating parameters according to the instrument manufacturer's instructions.

7.4 Operating conditions: The analyst should follow the instructions provided by the instrument manufacturer. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. This must be verified by analyzing a tuning solution (Section 5.8) at least four times with relative standard deviations of $\leq$ 5% for the analytes contained in the tuning solution.

> NOTE: Precautions must be taken to protect the channel electron multiplier from high ion currents. The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing, which invalidates the calibration curve, causes instability, and invalidates sample analyses.

7.5 Conduct mass calibration and resolution checks in the mass regions of interest. The mass calibration and resolution parameters are required criteria which must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be less than 0.9 amu full width at 10 percent peak height.

7.6 Calibrate the instrument for the analytes of interest (recommended isotopes for the analytes in Table 1 are provided in Table 3), using the calibration blank and at least a single initial calibration standard according to the instrument manufacturer's procedure. Flush the system with the rinse blank (5.5.3) between each standard solution. Use the average of at leastthree integrations for both calibration and sample analyses.

7.7 All masses which could affect data quality should be monitored to determine potential effects from matrix components on the analyte peaks. The recommended isotopes to be monitored are liste in Table 3.

7.8 Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the calibration verification solution (Section 5.7). When measurements exceed

± 10% of the accepted value, the analyses must be terminated, the problem corrected, the instrument recalibrated, and the new calibration verified. Any samples analyzed under an out-of-control calibration must be reanalyzed. During the course of an analytical run, the instrument may be "resloped" or recalibrated to correct for instrument drift. A recalibration must then be followed immediately by a new analysis of a CCV and CCB before any further samples may be analyzed.

7.9 Flush the system with the rinse blank solution (5.5.3) until the signal levels return to the method's levels of quantitation (usually about 30 seconds) before the analysis of each sample (see Section 7.7). Nebulize each sample until a steady-state signal is achieved (usually about 30 seconds) prior to collecting data. Analyze the calibration verification solution (Section 5.6) and the calibration blank (Section 5.5.1) at a frequency of at least once every 10 analytical samples. Flow-injection systems may be used as long as they can meet the performance criteria of this method.

7.10 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte (or species needed for a correction) or measure an alternate less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration (see Sec. 7.6 and 7.8).

7.11 Calculations: The quantitative values shall be reported in appropriate units, such as micrograms per liter (µg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. If dilutions were performed, the appropriate corrections must be applied to the sample values.

7.11.1 If appropriate, or required, calculate results for solids on a dry-weight basis as follows:

(1) A separate determination of percent solids must be performed.

(2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry weight)(mg/kg)} = \frac{C \times V}{W \times S}$$

Where,

C = Digest Concentration (mg/L)
V = Final volume in liters after sample preparation
W = Weight in kg of wet sample

$$S = \frac{\%\ \text{Solids}}{100}$$

Calculations should include appropriate interference corrections (see Section 3.2 for examples), internal-standard normalization, and the

summation of signals at 206, 207, and 208 m/z for lead (to compensate for any differences in the abundances of these isotopes between samples and standards).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and be available for easy reference or inspection.

8.2 Instrument Detection Limits (IDLs) in µg/L can be estimated by calculating the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs must be determined at least every three months and kept with the instrument log book. Refer to Chapter One for additional guidance.

8.3 The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to fall between 30 and 120 percent of the intensity of that internal standard in the initial calibration standard, the following procedure is followed. The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. This procedure must be repeated until the internal-standard intensities fall within the prescribed window. The intensity levels of the internal standards for the calibration blank (Section 5.5.1) and instrument check standard (Section 5.6) must agree within ± 20 percent of the intensity level of the internal standard of the original calibration solution. If they do not agree, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

8.4 To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are such that, at the correction factor, the analyte is less than the limit of quantification and the concentration of interferents are insignificant, then the data may go uncorrected. Note that monitoring the interference sources does not necessarily require monitoring the interferant itself, but that a molecular species may be monitored to indicate the presence of the interferent. When correcttion equations are used, all QC criteria must also be met. Extensive QC for interference corrections are required at all times. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions could impact the analytes of interest. Unsuspected interferences may be detected by adding pure major matrix components to a sample to observe any impact on the analyte signals. When an interference source is present, the sample elements impacted must be flagged to indicate (a) the percentage interference correction applied to the data or (b) an uncorrected interference by virtue of the elemental equation used for quantitation. The isotope proportions for an element or molecular-ion cluster provide information useful for quality assurance.

NOTE: Only isobaric elemental, molecular, and doubly charged interference corrections which use the observed isotopic-response ratios or parent-to-oxide ratios (provided an oxide internal standard is used as described in Section 3.2) for each instrument system are acceptable corrections for use in Method 6020.

8.5 Dilution Test: If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration in the reagent blank, refer to Section 5.5.2), an analysis of a fivefold (1+4) dilution must agree within ± 10% of the original determination. If not, an interference effect must be suspected. One dilution test must be included for each twenty samples (or less) of each matrix in a batch.

8.6 Post-Digestion Spike Addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125 percent of the known value or within the laboratory derived acceptance criteria. The spike addition should be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample must be diluted and reanalyzed to compensate for the matrix effect. Results must agree to within 10% of the original determination. The use of a standard-addition analysis procedure may also be used to compensate for this effect (Refer to Method 7000).

8.7 A Laboratory Control Sample (LCS) should be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the test samples. One LCS should be prepared and analyzed for each sample batch at a frequency of one LCS for each 20 samples or less.

8.8 Check the instrument calibration by analyzing appropriate quality control solutions as follows:

8.8.1 Check instrument calibration using a calibration blank (Section 5.5.1) and the initial calibration verification solution (Sections 5.7 and 7.9).

8.8.2 Verify calibration at a frequency of every 10 analytical samples with the instrument check standard (Section 5.6) and the calibration blank (Section 5.5.1). These solutions must also be analyzed for each analyte at the beginning of the analysis and after the last sample.

8.8.3 The results of the initial calibration verification solution and the instrument check standard must agree within ± 10% of the expected value. If not, terminate the analysis, correct the problem, and recalibrate the instrument. Any sample analyzed under an out-of-control calibration must be reanalyzed .

8.8.4 The results of the calibration blank must be less than 3 times the current IDL for each element. If this is not the case, the reason for the out-of-control condition must be found and corrected, and

affected samples must be reanalyzed. If the laboratory consistently has concentrations greater than 3 times the IDL, the IDL may be indicative of an estimated IDL and should be re-evaluated.

8.9 Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hours, whichever is more frequent. Do this by analyzing the interference check solutions A and AB. The analyst should be aware that precipitation from solution AB may occur with some elements, specifically silver. Refer to Section 3.0 for a discussion on intereferences and potential solutions to those intereferences if additional guidance is needed.

8.10 Analyze one duplicate sample for every matrix in a batch at a frequency of one matrix duplicate for every 20 samples.

8.10.1 The relative percent difference (RPD) between duplicate determinations must be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (duplicate)

A control limit of 20% RPD should not be exceeded for analyte values greater than 100 times the instrumental detection limit. If this limit is exceeded, the reason for the out-of-control situation must be found and corrected, and any samples analyzed during the out-of-control condition must be reanalyzed.

9.0 METHOD PERFORMANCE

9.1 In an EPA multi-laboratory study, 10 laboratories applied the ICP-MS technique to both aqueous and solid samples. TABLE 4 summarizes the method performance data for aqueous samples. Performance data for solid samples is provided in TABLE 5.

10.0 REFERENCES

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TABLE 1. ELEMENTS APPROVED FOR ICP-MS DETERMINATION

Element	CAS* #
Aluminum	7429-90-5
Antimony	7440-36-0
Arsenic	7440-38-2
Barium	7440-39-3
Beryllium	7440-41-7
Cadmium	7440-43-9
Chromium	7440-47-3
Cobalt	7440-48-4
Copper	7440-50-8
Lead	7439-92-1
Manganese	7439-96-5
Nickel	7440-02-0
Silver	7440-22-4
Thallium	7440-28-0
Zinc	7440-66-6

TABLE 2. RECOMMENDED INTERFERENCE CHECK SAMPLE COMPONENTS AND CONCENTRATIONS

Solution component	Solution A Concentration (mg/L)	Solution AB Concentration(mg/L)
Al	100.0	100.0
Ca	100.0	100.0
Fe	100.0	100.0
Mg	100.0	100.0
Na	100.0	100.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	1000.0	1000.0
Mo	2.0	2.0
Ti	2.0	2.0
As	0.0	0.0200
Cd	0.0	0.0200
Cr	0.0	0.0200
Co	0.0	0.0200
Cu	0.0	0.0200
Mn	0.0	0.0200
Ni	0.0	0.0200
Ag	0.0	0.0200
Zn	0.0	0.0200

TABLE 3. RECOMMENDED ISOTOPES FOR SELECTED ELEMENTS

Mass	Element of interest
27	Aluminum
121, **123**	Antimony
75	Arsenic
138, 137, 136, **135**, 134	Barium
9	Beryllium
209	Bismuth (IS)
114, 112, **111**, 110, 113, 116, 106	Cadmium
42, 43, **44**, 46, 48	Calcium (I)
35, 37, (77, 82)[a]	Chlorine (I)
52, **53**, **50**, 54	Chromium
59	Cobalt
63, **65**	Copper
165	Holmium (IS)
115, 113	Indium (IS)
56, **54**, **57**, 58	Iron (I)
139	Lanthanum (I)
208, **207**, **206**, 204	Lead
6[b], 7	Lithium (IS)
24, **25**, **26**	Magnesium (I)
55	Manganese
98, 96, 92, **97**, 94, (108)[a]	Molybdenum (I)
58, **60**, 62, **61**, 64	Nickel
39	Potassium (I)
103	Rhodium (IS)
45	Scandium (IS)
107, **109**	Silver
23	Sodium (I)
159	Terbium (IS)
205, 203	Thallium
120, **118**	Tin (I)
89	Yttrium (IS)
64, **66**, **68**, **67**, 70	Zinc

NOTE: Method 6020 is recommended for only those analytes listed in Table 1. Other elements are included in this table because they are potential interferents (labeled I) in the determination of recommended analytes, or because they are commonly used internal standards (labeled IS). Isotopes are listed in descending order of natural abundance. The most generally useful isotopes are underlined and in boldface, although certain matrices may require the use of alternative isotopes. [a] These masses are also useful for interference correction (Section 3.2). [b] Internal standard must be enriched in the ^{6}Li isotope. This minimizes interference from indigenous lithium.

TABLE 4. ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR AQUEOUS SOLUTIONS

Element	Comparability[a] Range	%RSD Range	N[b]	S[c]
Aluminum	95 - 100	11 - 14	14 - 14	4
Antimony	d	5.0 - 7.6	16 - 16	3
Arsenic	97 - 114	7.1 - 48	12 - 14	4
Barium	91 - 99	4.3 - 9.0	16 - 16	5
Beryllium	103 - 107	8.6 - 14	13 - 14	3
Cadmium	98 - 102	4.6 - 7.2	18 - 20	3
Calcium	99 - 107	5.7 - 23	17 - 18	5
Chromium	95 - 105	13 - 27	16 - 18	4
Cobalt	101 - 104	8.2 - 8.5	18 - 18	3
Copper	85 - 101	6.1 - 27	17 - 18	5
Iron	91 - 900	11 - 150	10 - 12	5
Lead	71 - 137	11 - 23	17 - 18	6
Magnesium	98 - 102	10 - 15	16 - 16	5
Manganese	95 - 101	8.8 - 15	18 - 18	4
Nickel	98 - 101	6.1 - 6.7	18 - 18	2
Potassium	101 - 114	9.9 - 19	11 - 12	5
Selenium	102 - 107	15 - 25	12 - 12	3
Silver	104 - 105	5.2 - 7.7	13 - 16	2
Sodium	82 - 104	24 - 43	9 - 10	5
Thallium	88 - 97	9.7 - 12	18 - 18	3
Vanadium	107 - 142	23 - 68	8 - 13	3
Zinc	93 - 102	6.8 - 17	16 - 18	5

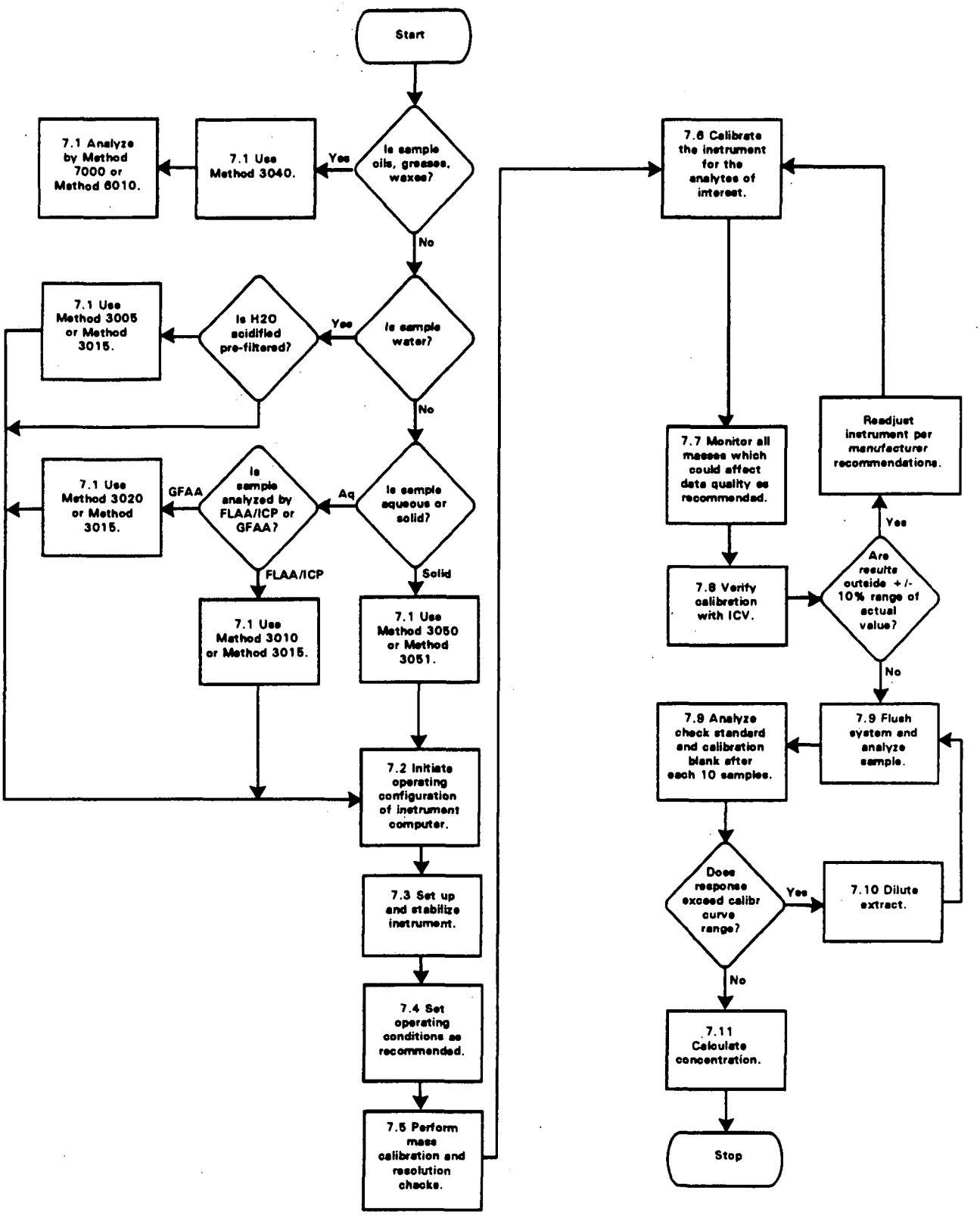
[a] Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique. [b] N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value). [c] S is the number of samples with results greater than the limit of quantitation. [d] No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

TABLE 5. ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR SOLID MATRICES

Element	Comparability[a] Range	%RSD Range	N[b]	S[c]
Aluminum	83 - 101	11 - 39	13 - 14	7
Antimony	d	12 - 21	15 - 16	2
Arsenic	79 - 102	12 - 23	16 - 16	7
Barium	100 - 102	4.3 - 17	15 - 16	7
Beryllium	50 - 87	19 - 34	12 - 14	5
Cadmium	93 - 100	6.2 - 25	19 - 20	5
Calcium	95 - 109	4.1 - 27	15 - 17	7
Chromium	77 - 98	11 - 32	17 - 18	7
Cobalt	43 - 102	15 - 30	17 - 18	6
Copper	90 - 109	9.0 - 25	18 - 18	7
Iron	87 - 99	6.7 - 21	12 - 12	7
Lead	90 - 104	5.9 - 28	15 - 18	7
Magnesium	89 - 111	7.6 - 37	15 - 16	7
Manganese	80 - 108	11 - 40	16 - 18	7
Nickel	87 - 117	9.2 - 29	16 - 18	7
Potassium	97 - 137	11 - 62	10 - 12	5
Selenium	81	39	12	1
Silver	43 - 112	12 - 33	15 - 15	3
Sodium	100 - 146	14 - 77	8 - 10	5
Thallium	91	33	18	1
Vanadium	83 - 147	20 - 70	6 - 14	7
Zinc	84 - 124	14 - 42	18 - 18	7

[a] Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique. [b] N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value). [c] S is the number of samples with results greater than the limit of quantitation. [d] No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

METHOD 6020
INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY



METHOD 7000A

ATOMIC ABSORPTION METHODS

1.0 SCOPE AND APPLICATION

1.1 Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters and domestic and industrial wastes. While drinking water free of particulate matter may be analyzed directly, ground water, other aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion prior to analysis for both total and acid leachable metals. Analysis for dissolved elements does not require digestion if the sample has been filtered and acidified.

1.2 Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and models of atomic absorption spectrophotometers. The data shown in Table 1 provide some indication of the detection limits obtainable by direct aspiration and by furnace techniques. For clean aqueous samples, the detection limits shown in the table by direct aspiration may be extended downward with scale expansion and upward by using a less sensitive wavelength or by rotating the burner head. Detection limits by direct aspiration may also be extended through concentration of the sample and/or through solvent extraction techniques. For certain samples, lower concentrations may also be determined using the furnace techniques. The detection limits given in Table 1 are somewhat dependent on equipment (such as the type of spectrophotometer and furnace accessory, the energy source, the degree of electrical expansion of the output signal), and are greatly dependent on sample matrix. Detection limits should be established, empirically, for each matrix type analyzed. When using furnace techniques, however, the analyst should be cautioned as to possible chemical reactions occurring at elevated temperatures which may result in either suppression or enhancement of the analysis element. To ensure valid data with furnace techniques, the analyst must examine each matrix for interference effects (see Step 3.2.1) and, if detected, treat them accordingly, using either successive dilution, matrix modification, or method of standard additions (see Step 8.7).

1.3 Where direct-aspiration atomic absorption techniques do not provide adequate sensitivity, reference is made to specialized procedures (in addition to the furnace procedure) such as the gaseous-hydride method for arsenic and selenium and the cold-vapor technique for mercury.

2.0 SUMMARY OF METHOD

2.1 Although methods have been reported for the analysis of solids by atomic absorption spectroscopy, the technique generally is limited to metals in solution or solubilized through some form of sample processing.

2.2 Preliminary treatment of waste water, ground water, EP extracts, and industrial waste is always necessary because of the complexity and variability of sample matrix. Solids, slurries, and suspended material must be subjected to a solubilization process before analysis. This process may vary because of the

metals to be determined and the nature of the sample being analyzed. Solubilization and digestion procedures are presented in Step 3.2 (Sample Preparation Methods).

2.3 In direct-aspiration atomic absorption spectroscopy, a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp or an electrodeless discharge lamp is directed through the flame into a monochromator, and onto a detector that measures the amount of absorbed light. Absorption depends upon the presence of free unexcited ground-state atoms in the flame. Because the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

2.4 When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. As a greater percentage of available analyte atoms is vaporized and dissociated for absorption in the tube rather than the flame, the use of smaller sample volumes or detection of lower concentrations of elements is possible. The principle is essentially the same as with direct aspiration atomic absorption, except that a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground-state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground-state element in the vapor. The metal atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace, thereby causing the injected specimen to be volatilized. A monochromator isolates the characteristic radiation from the hollow cathode lamp or electrodeless discharge lamp, and a photosensitive device measures the attenuated transmitted radiation.

3.0 INTERFERENCES

3.1 Direct aspiration

3.1.1 The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or when the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome phosphate interference in magnesium, calcium, and barium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

3.1.2 Chemical interferences may also be eliminated by separating the metal from the interfering material. Although complexing agents are employed primarily to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

3.1.3 The presence of high dissolved solids in the sample may result in an interference from nonatomic absorbance such as light scattering. If background correction is not available, a nonabsorbing wavelength should be checked. Preferably, samples containing high solids should be extracted.

3.1.4 Ionization interferences occur when the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positively charged ion. This type of interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess (1,000 mg/L) of an easily ionized element such as K, Na, Li or Cs.

3.1.5 Spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Interference can also occur when resonant energy from another element in a multielement lamp, or from a metal impurity in the lamp cathode, falls within the bandpass of the slit setting when that other metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

3.1.6 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

3.1.7 All metals are not equally stable in the digestate, especially if it contains only nitric acid, not nitric acid and hydrochloric acid. The digestate should be analyzed as soon as possible, with preference given to Sn, Sb, Mo, Ba, and Ag.

3.2 Furnace procedure

3.2.1 Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical interferences. The composition of the sample matrix can have a major effect on the analysis. It is those effects which must be determined and taken into consideration in the analysis of each different matrix encountered. To help verify the absence of matrix or chemical interference, the serial dilution technique (see Step 8.6) may be used. Those samples which indicate the presence of interference should be treated in one or more of the following ways:

1. Successively dilute and reanalyze the samples to eliminate interferences.

2. Modify the sample matrix either to remove interferences or to stabilize the analyte. Examples are the addition of ammonium nitrate to remove alkali chlorides and the addition of ammonium phosphate to retain cadmium. The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation.

3. Analyze the sample by method of standard additions while noticing the precautions and limitations of its use (see Step 8.7.2).

3.2.2 Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, use either background correction or choose an alternate wavelength. Background correction may also compensate for nonspecific broad-band absorption interference.

3.2.3 Continuum background correction cannot correct for all types of background interference. When the background interference cannot be compensated for, chemically remove the analyte or use an alternate form of background correction, e.g., Zeeman background correction.

3.2.4 Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the analyte.

3.2.5 Samples containing large amounts of organic materials should be oxidized by conventional acid digestion before being placed in the furnace. In this way, broad-band absorption will be minimized.

3.2.6 Anion interference studies in the graphite furnace indicate that, under conditions other than isothermal, the nitrate anion is preferred. Therefore, nitric acid is preferable for any digestion or solubilization step. If another acid in addition to nitric acid is required, a minimum amount should be used. This applies particularly to hydrochloric and, to a lesser extent, to sulfuric and phosphoric acids.

3.2.7 Carbide formation resulting from the chemical environment of the furnace has been observed. Molybdenum may be cited as an example. When carbides form, the metal is released very slowly from the resulting metal carbide as atomization continues. Molybdenum may require 30 seconds or more atomization time before the signal returns to baseline levels. Carbide formation is greatly reduced and the sensitivity increased with the use of pyrolytically coated graphite. Elements that readily form carbides are noted with the symbol (p) in Table 1.

3.2.8 For comments on spectral interference, see Step 3.1.5.

3.2.9 Cross-contamination and contamination of the sample can be major sources of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned as directed in Step 4.8. Pipet tips are a frequent source of contamination. If suspected, they should be acid soaked with 1:5 nitric acid and rinsed thoroughly with tap and reagent water. The use of a better grade of pipet tip can greatly reduce this problem. Special attention should be given to reagent blanks in both analysis and in the correction of analytical results. Lastly, pyrolytic graphite, because of the production process and handling, can become contaminated. As many as five to ten high-temperature burns may be required to clean the tube before use.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer - Single- or dual-channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a graphical display.

4.2 Burner - The burner recommended by the particular instrument manufacturer should be used. For certain elements the nitrous oxide burner is required.

4.3 Hollow cathode lamps - Single-element lamps are preferred but multielement lamps may be used. Electrodeless discharge lamps may also be used when available. Other types of lamps meeting the performance criteria of this method may be used.

4.4 Graphite furnace - Any furnace device capable of reaching the specified temperatures is satisfactory.

4.5 Graphical display and recorder - A recorder is recommended for furnace work so that there will be a permanent record and that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, peak shape, etc., can be easily recognized.

4.6 Pipets - Microliter, with disposable tips. Sizes can range from 5 to 100 uL as required. Pipet tips should be checked as a possible source of contamination prior to their use. The accuracy of automatic pipets must be verified daily. Class A pipets can be used for the measurement of volumes larger than 1 mL.

4.7 Pressure-reducing valves - The supplies of fuel and oxidant should be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

4.8 Glassware - All glassware, polypropylene, or Teflon containers, including sample bottles, flasks and pipets, should be washed in the following sequence: detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and reagent water. (Chromic acid should not be used as a cleaning agent for glassware if chromium is to be included in the analytical scheme.) If it can be documented through an active analytical quality control program using spiked samples and reagent blanks that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use

without lessening the accuracy of the determination. All reagents should be analyzed to provide proof that all constituents are below the MDLs.

5.2 Reagent water. All references to water in this method refer to reagent water unless otherwise specified. Reagent grade water will be of at least 16 Mega Ohm quality.

5.3 Nitric acid (concentrated), HNO_3. Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with water by adding the concentrated acid to an equal volume of water. If the reagent blank is less than the IDL, the acid may be used.

5.4 Hydrochloric acid (1:1), HCl. Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with water by adding the concentrated acid to an equal volume of water. If the reagent blank is less than the IDL, the acid may be used.

5.5 Fuel and oxidant - High purity acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or a cylinder of compressed air and should be clean and dry. Nitrous oxide is also required for certain determinations. Standard, commercially available argon and nitrogen are required for furnace work.

5.6 Stock standard metal solutions - Stock standard solutions are prepared from high purity metals, oxides, or nonhygroscopic salts using water and redistilled nitric or hydrochloric acids. (See individual methods for specific instructions.) Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1,000 mg of the metal per liter. Commercially available standard solutions may also be used. Where the sample viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) may be used (see Step 8.7).

5.7 Calibration standards - For those instruments which do not read out directly in concentration, a calibration curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of standards which produce an absorbance of 0.0 to 0.7. Calibration standards are prepared by diluting the stock metal solutions at the time of analysis. For best results, calibration standards should be prepared fresh each time a batch of samples is analyzed. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range of the linear part of the curve. The calibration standards should be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following processing. Beginning with the blank and working toward the highest standard, aspirate the solutions and record the readings. Repeat the operation with both the calibration standards and the samples a sufficient number of times to secure a reliable average reading for each solution. Calibration standards for furnace procedures should be prepared as described on the individual sheets for that metal. Calibration curves are always required.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material in Chapter Three, Metallic Analytes.

7.0 PROCEDURE

7.1 Preliminary treatment of waste water, ground water, EP extracts, and industrial waste is always necessary because of the complexity and variability of sample matrices. Solids, slurries, and suspended material must be subjected to a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. Solubilization and digestion procedures are presented in Chapter Three, Step 3.2, Sample Preparation Methods. Samples which are to be analyzed for dissolved constituents need not be digested if they have been filtered and acidified.

7.2 Direct aspiration (flame) procedure

7.2.1 Differences between the various makes and models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the manufacturer's operating instructions for a particular instrument. In general, after choosing the proper lamp for the analysis, allow the lamp to warm up for a minimum of 15 minutes, unless operated in a double-beam mode. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the current according to the manufacturer's recommendation. Subsequently, light the flame and regulate the flow of fuel and oxidant. Adjust the burner and nebulizer flow rate for maximum percent absorption and stability. Balance the photometer. Run a series of standards of the element under analysis. Construct a calibration curve by plotting the concentrations of the standards against absorbances. Set the curve corrector of a direct reading instrument to read out the proper concentration. Aspirate the samples and determine the concentrations either directly or from the calibration curve. Standards must be run each time a sample or series of samples is run.

7.3 Furnace procedure

7.3.1 Furnace devices (flameless atomization) are a most useful means of extending detection limits. Because of differences between various makes and models of satisfactory instruments, no detailed operating instructions can be given for each instrument. Instead, the analyst should follow the instructions provided by the manufacturer of a particular instrument.

7.3.2 Background correction is important when using flameless atomization, especially below 350 nm. Certain samples, when atomized, may absorb or scatter light from the lamp. This can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high. Zeeman background correction is effective in overcoming composition or structured background

interferences. It is particularly useful when analyzing for As in the presence of Al and when analyzing for Se in the presence of Fe.

7.3.3 Memory effects occur when the analyte is not totally volatilized during atomization. This condition depends on several factors: volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization, and furnace design. This situation is detected through blank burns. The tube should be cleaned by operating the furnace at full power for the required time period, as needed, at regular intervals during the series of determinations.

7.3.4 Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.3.5 To verify the absence of interference, follow the serial dilution procedure given in Step 8.6.

7.3.6 A check standard should be run after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced. Tube life depends on sample matrix and atomization temperature. A conservative estimate would be that a tube will last at least 50 firings. A pyrolytic coating will extend that estimated life by a factor of three.

7.4 Calculation

7.4.1 For determination of metal concentration by direct aspiration and furnace: Read the metal value from the calibration curve or directly from the read-out system of the instrument.

7.4.2 If dilution of sample was required:

$$\text{ug/L metal in sample} = A \left(\frac{C + B}{C}\right)$$

where:

A = ug/L of metal in diluted aliquot from calibration curve.
B = Acid blank matrix used for dilution, mL.
C = Sample aliquot, mL.

7.4.3 For solid samples, report all concentrations in consistent units based on wet weight. Hence:

$$\text{ug metal/kg sample} = \frac{A \times V}{W}$$

where:

A = ug/L of metal in processed sample from calibration curve.
V = Final volume of the processed sample, mL.
W = Weight of sample, grams.

7.4.4 Different injection volumes must not be used for samples and standards. Instead, the sample should be diluted and the same size injection volume be used for both samples and standards. If dilution of the sample was required:

$$\text{ug/L of metal in sample} = Z \left(\frac{C + B}{C} \right)$$

where:

Z = ug/L of metal read from calibration curve or read-out system.
B = Acid blank matrix used for dilution mL.
C = Sample aliquot, mL.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 A calibration curve must be prepared each day with a minimum of a calibration blank and three standards. After calibration, the calibration curve must be verified by use of at least a calibration blank and a calibration check standard (made from a reference material or other independent standard material) at or near the mid-range. The calibration reference standard must be measured within 10 % of it's true value for the curve to be considered valid.

8.3 If more than 10 samples per day are analyzed, the working standard curve must be verified by measuring satisfactorily a mid-range standard or reference standard after every 10 samples. This sample value must be within 20% of the true value, or the previous ten samples need to be reanalyzed.

8.4 At least one matrix spike and one matrix spike duplicate sample shall be included in each analytical batch. A laboratory control sample shall also be processed with each sample batch. Refer to Chapter One for more information.

8.5 Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) is recommended (see Section 8.7 below). Section 8.6 provides tests to evaluate the need for using the MSA.

8.6 Interference tests

8.6.1 Dilution test - For each analytical batch select one typical sample for serial dilution to determine whether interferences are present. The concentration of the analyte should be at least 25 times the estimated detection limit. Determine the apparent concentration in the undiluted sample. Dilute the sample by a minimum of five fold (1+4) and reanalyze. If all of the samples in the batch are below 10 times the detection limits, perform the spike recovery analysis described below. Agreement within 10% between the concentration for the undiluted sample and five times the concentration for the diluted sample indicates the absence of interferences, and such samples may be analyzed without using the method of standard additions.

8.6.2 Recovery test - If results from the dilution test do not agree, a matrix interference may be suspected and a spiked sample should be analyzed to help confirm the finding from the dilution test. Withdraw another aliquot of the test sample and add a known amount of analyte to bring the concentration of the analyte to 2 to 5 times the original concentration. If all of the samples in the batch have analyte concentrations below the detection limit, spike the selected sample at 20 times the detection limit. Analyze the spiked sample and calculate the spike recovery. If the recovery is less than 85% or greater than 115%, the method of standard additions shall be used for all samples in the batch.

8.7 Method of standard additions - The standard addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The method of standard additions shall be used for analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

8.7.1 The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a known volume V_S of a standard analyte solution of concentration C_S. To the second aliquot (labeled B) is added the same volume V_S of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration C_x is calculated:

$$C_x = \frac{S_B V_S C_S}{(S_A - S_B) V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and C_s should be chosen so that S_A is roughly twice S_B on the average, avoiding excess dilution of the sample. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

8.7.2 Improved results can be obtained by employing a series of standard additions. To equal volumes of the sample are added a series of standard solutions containing different known quantities of the analyte, and all solutions are diluted to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50 percent of the expected absorbance from the endogenous analyte in the sample. Additions 2 and 3 should be prepared so that the concentrations are approximately 100 and 150 percent of the expected endogenous sample absorbance. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the

ordinate. An example of a plot so obtained is shown in Figure 1. A linear regression program may be used to obtain the intercept concentration.

8.7.3 For the results of this MSA technique to be valid, the following limitations must be taken into consideration:

1. The apparent concentrations from the calibration curve must be linear over the concentration range of concern. For the best results, the slope of the MSA plot should be nearly the same as the slope of the standard curve. If the slope is significantly different (greater than 20%), caution should be exercised.

2. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

3. The determination must be free of spectral interference and corrected for nonspecific background interference.

8.8 All quality control measures described in Chapter One should be followed.

9.0 METHOD PERFORMANCE

9.1 See individual methods.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.

2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

3. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

TABLE 1.
ATOMIC ABSORPTION CONCENTRATION RANGES

Metal	Direct Aspiration Detection Limit (mg/L)	Direct Aspiration Sensitivity (mg/L)	Furnace Procedure[a,c] Detection Limit (ug/L)
Aluminum	0.1	1	--
Antimony	0.2	0.5	3
Arsenic[b]	0.002	--	1
Barium	0.1	0.4	2
Beryllium	0.005	0.025	0.2
Cadmium	0.005	0.025	0.1
Calcium	0.01	0.08	--
Chromium	0.05	0.25	1
Cobalt	0.05	0.2	1
Copper	0.02	0.1	1
Iron	0.03	0.12	1
Lead	0.1	0.5	1
Lithium	0.002	0.04	--
Magnesium	0.001	0.007	--
Manganese	0.01	0.05	0.2
Mercury[d]	0.0002	--	--
Molybdenum(p)	0.1	0.4	1
Nickel	0.04	0.15	--
Osmium	0.03	1	--
Potassium	0.01	0.04	--
Selenium[b]	0.002	--	2
Silver	0.01	0.06	0.2
Sodium	0.002	0.015	--
Strontium	0.03	0.15	--
Thallium	0.1	0.5	1
Tin	0.8	4	--
Vanadium(p)	0.2	0.8	4
Zinc	0.005	0.02	0.05

NOTE: The symbol (p) indicates the use of pyrolytic graphite with the furnace procedure.

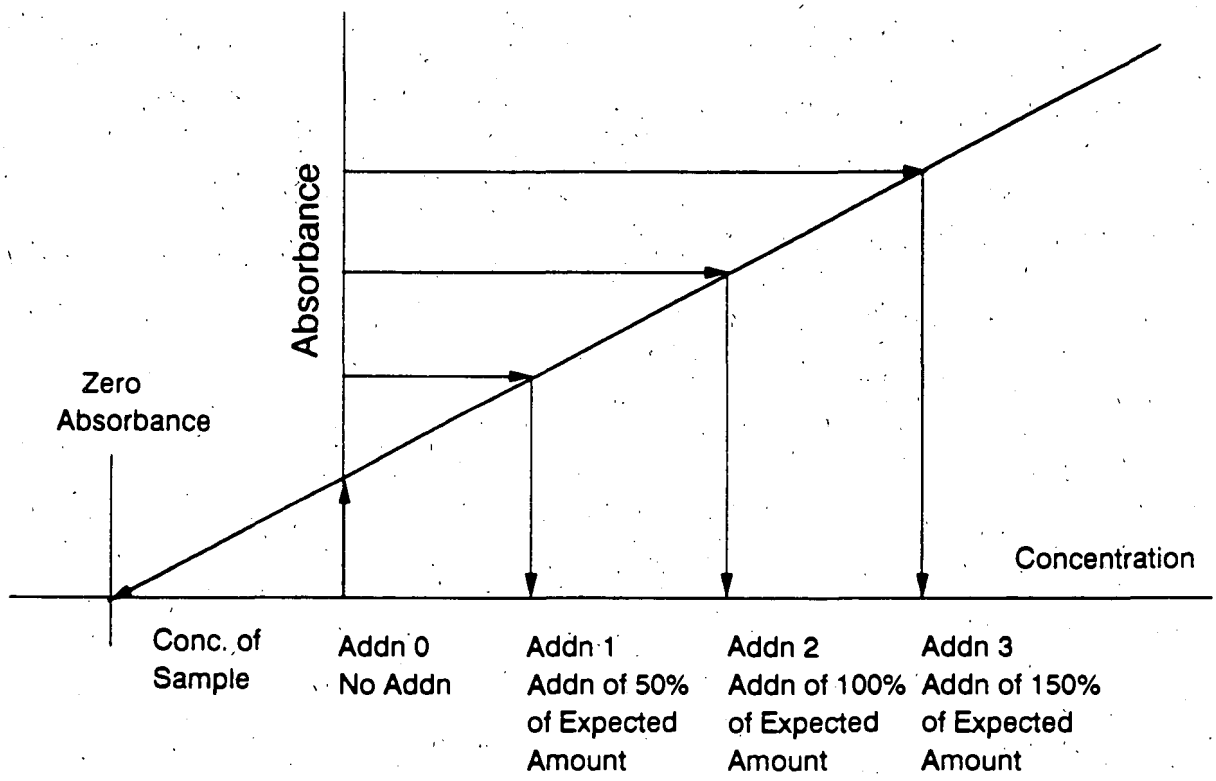
[a]For furnace sensitivity values, consult instrument operating manual.

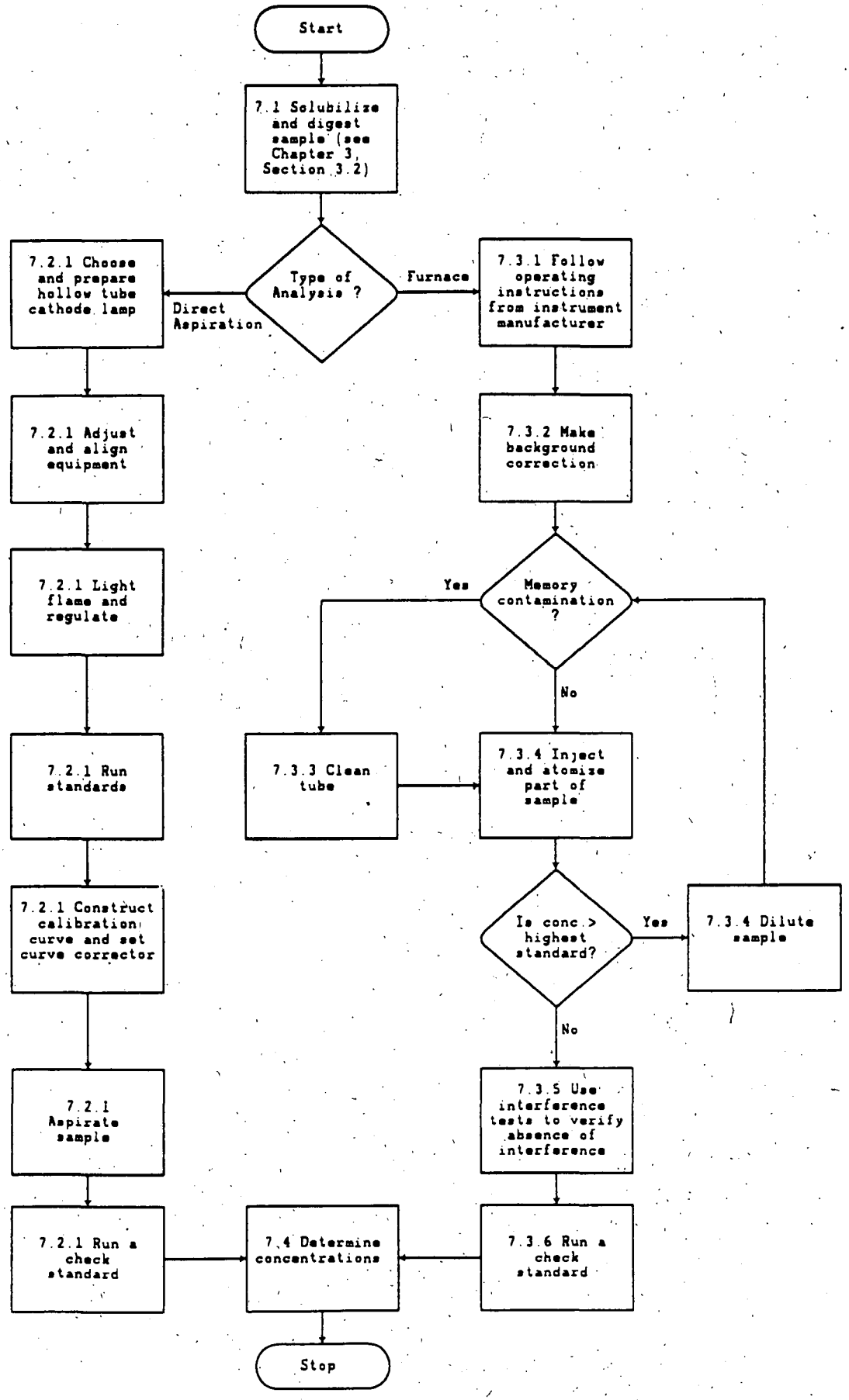
[b]Gaseous hydride method.

[c]The listed furnace values are those expected when using a 20-uL injection and normal gas flow, except in the cases of arsenic and selenium, where gas interrupt is used.

[d]Cold vapor technique.

FIGURE 1.
STANDARD ADDITION PLOT




Start
7.1 Solubilize and digest sample (see Chapter 3, Section 3.2)
Type of Analysis ?
Direct Aspiration
Furnace
7.2.1 Choose and prepare hollow tube cathode lamp
7.2.1 Adjust and align equipment
7.2.1 Light flame and regulate
7.2.1 Run standards
7.2.1 Construct calibration curve and set curve corrector
7.2.1 Aspirate sample
7.2.1 Run a check standard
7.3.1 Follow operating instructions from instrument manufacturer
7.3.2 Make background correction
Memory contamination ?
Yes
No
7.3.3 Clean tube
7.3.4 Inject and atomize part of sample
Is conc > highest standard?
Yes
7.3.4 Dilute sample
No
7.3.5 Use interference tests to verify absence of interference
7.3.6 Run a check standard
7.4 Determine concentrations
Stop

METHOD 7060

ARSENIC (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7060 is an atomic absorption procedure approved for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7060, samples must be prepared in order to convert organic forms of arsenic to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050.

2.2 Following the appropriate dissolution of the sample, a representative aliquot of the digestate is spiked with a nickel nitrate solution and is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode or EDL radiation during atomization will be proportional to the arsenic concentration.

2.3 The typical detection limit for this method is 1 ug/L.

3.0 INTERFERENCES

3.1 Elemental arsenic and many of its compounds are volatile; therefore, samples may be subject to losses of arsenic during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A nickel nitrate solution must be added to all digestates prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, arsenic analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Arsenic analysis is particularly susceptible to these problems because of its low analytical wavelength (193.7 nm). Simultaneous background

correction must be employed to avoid erroneously high results. Aluminum is a severe positive interferent in the analysis of arsenic, especially using D_2 arc background correction. Zeeman background correction is very useful in this situation.

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected by means of blank burns, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beaker: 250 mL.

4.2 Volumetric flasks: 10-mL.

4.3 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip-chart recorder.

4.4 Arsenic hollow cathode lamp, or electrodeless discharge lamp (EDL): EDLs provide better sensitivity for arsenic analysis.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Strip-chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1,000 uL, as required.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If a method blank using the acid is <MDL, the acid can be used.

5.3. Hydrogen peroxide (30%): Oxidant should be analyzed to determine levels of impurities. If a method blank using the H_2O_2 is <MDL, the acid can be used.

5.4 Arsenic standard stock solution (1,000 mg/L): Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.320 g of arsenic trioxide (As_2O_3, analytical reagent grade) or equivalent in 100 mL of Type II water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 liter (1 mL = 1 mg As).

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ or equivalent in Type II water and dilute to 100 mL.

5.6 Nickel nitrate solution (1%): Dilute 20 mL of the 5% nickel nitrate to 100 mL with Type II water.

5.7 Arsenic working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add 1 mL of concentrated HNO_3, 2 mL of 30% H_2O_2, and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with Type II water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile arsenic compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Paragraphs 7.1.1-7.1.3. Sludge-type samples should be prepared according to Method 3050. The applicability of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer 100 mL of well-mixed sample to a 250-mL Griffin beaker; add 2 mL of 30% H_2O_2 and sufficient concentrated HNO_3 to result in an acid concentration of 1% (v/v). Heat for 1 hr at 95°C or until the volume is slightly less than 50 mL.

7.1.2 Cool and bring back to 50 mL with Type II water.

7.1.3 Pipet 5 mL of this digested solution into a 10-mL volumetric flask, add 1 mL of the 1% nickel nitrate solution, and dilute to 10 mL with Type II water. The sample is now ready for injection into the furnace.

7.2 The 193.7-nm wavelength line and a background correction system are required. Follow the manufacturer's suggestions for all other spectrophotometer parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.5 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions.

7.6 Run a check standard after every 10 injections of samples. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.7 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased samples must be appropriately qualified (e.g., 5 ug/g aqueous phase).

7.8 Duplicates, spiked samples, and check standards should be routinely analyzed.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 20 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 206.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The optimal concentration range for this method is 5-100 ug/L.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

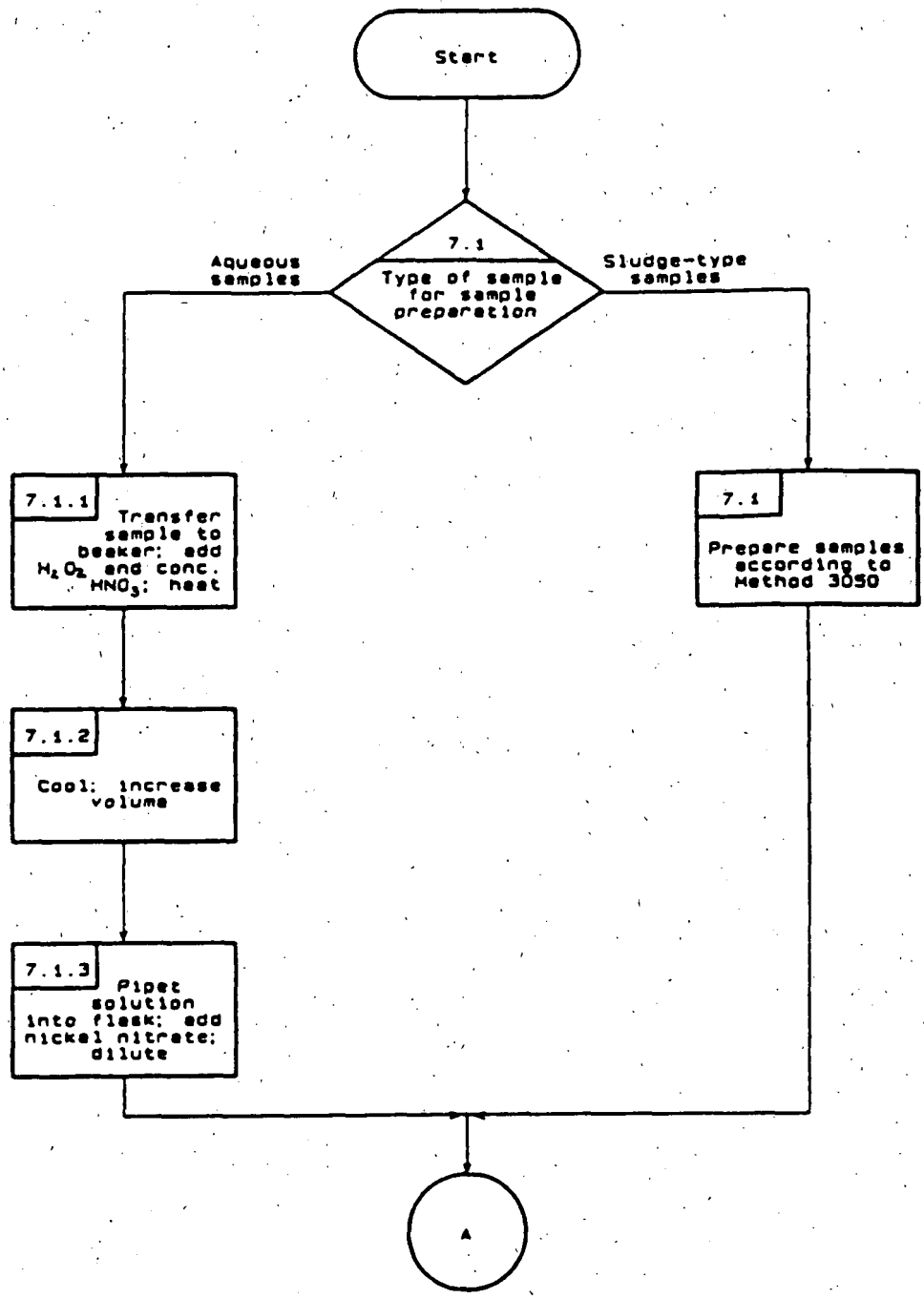
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.2.

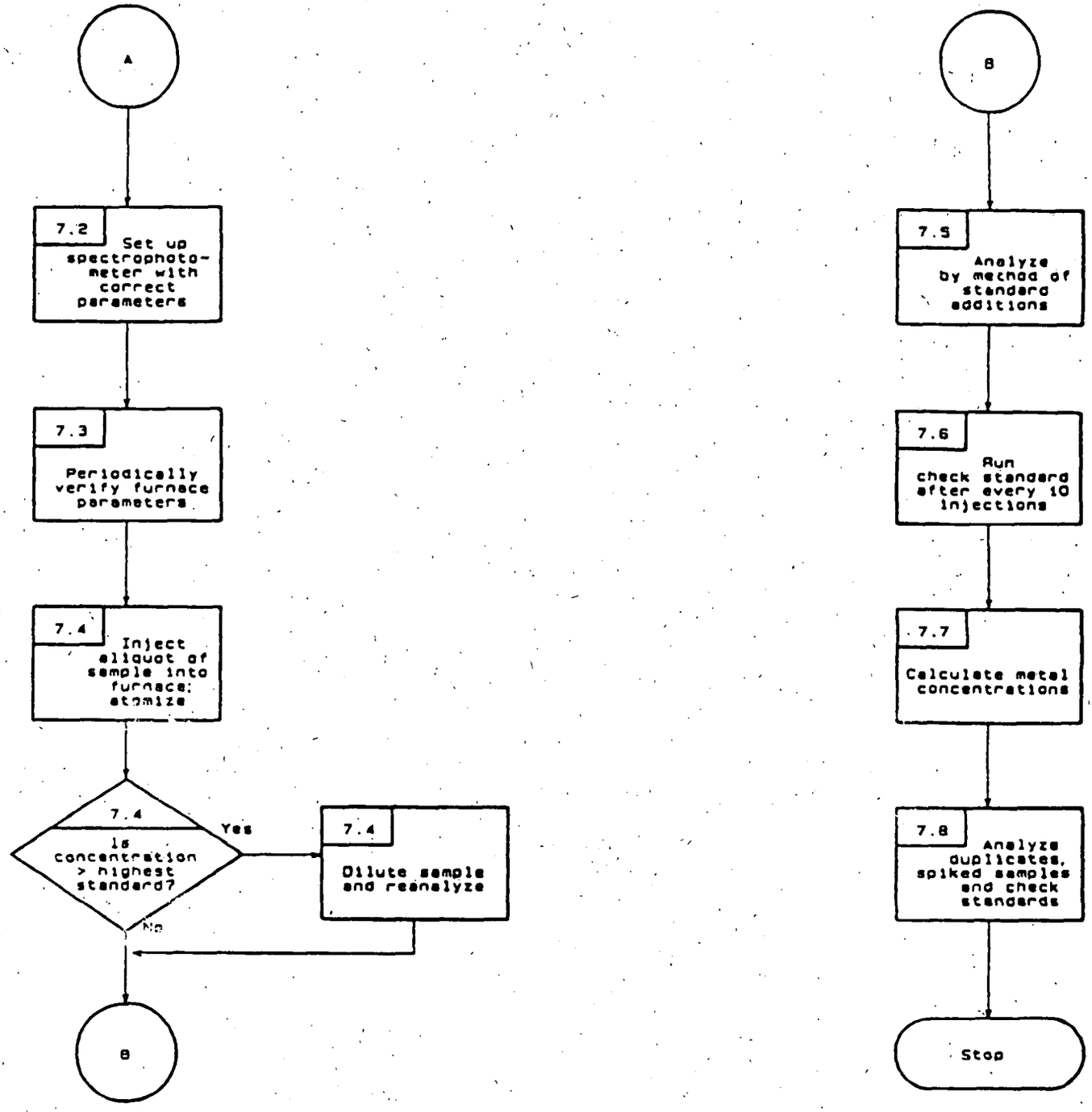
2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Contaminated soil	3050	2.0, 1.8 ug/g
Oily soil	3050	3.3, 3.8 ug/g
NBS SRM 1646 Estuarine sediment	3050	8.1, 8.33 ug/g[a]
Emission control dust	3050	430, 350 ug/g

[a]Bias of -30 and -28% from expected, respectively.


Start
7.1
Type of sample for sample preparation
Aqueous samples
Sludge-type samples
7.1.1
Transfer sample to beaker; add H_2O_2 and conc. HNO_3; heat
7.1.2
Cool; increase volume
7.1.3
Pipet solution into flask; add nickel nitrate; dilute
7.1
Prepare samples according to Method 3050
A


A
7.2
Set up spectrophotometer with correct parameters
7.3
Periodically verify furnace parameters
7.4
Inject aliquot of sample into furnace; atomize
7.4
Is concentration > highest standard?
Yes
No
7.4
Dilute sample and reanalyze
B
B
7.5
Analyze by method of standard additions
7.6
Run check standard after every 10 injections
7.7
Calculate metal concentrations
7.8
Analyze duplicates, spiked samples and check standards
Stop

METHOD 7060A

ARSENIC (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7060 is an atomic absorption procedure approved for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7060, samples must be prepared in order to convert organic forms of arsenic to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050.

2.2 Following the appropriate dissolution of the sample, a representative aliquot of the digestate is spiked with a nickel nitrate solution and is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode or EDL radiation during atomization will be proportional to the arsenic concentration. Other modifiers may be used in place of nickel nitrate if the analyst documents the chemical and concentration used.

2.3 The typical detection limit for water samples using this method is 1 ug/L. This detection limit may not be achievable when analyzing waste samples.

3.0 INTERFERENCES

3.1 Elemental arsenic and many of its compounds are volatile; therefore, samples may be subject to losses of arsenic during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A matrix modifier such as nickel nitrate must be added to all digestates prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, arsenic analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Arsenic analysis is particularly susceptible to these problems because of its low analytical wavelength (193.7 nm). Simultaneous background correction must be employed to avoid erroneously high results. Aluminum is a severe positive interferent in the analysis of arsenic, especially using D_2 arc background

correction. Although Zeeman background correction is very useful in this situation, use of any appropriate background correction technique is acceptable.

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected by means of blank burns, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beaker or equivalent: 250 mL.

4.2 Class A Volumetric flasks: 10-mL.

4.3 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photo-multiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a suitable recording device.

4.4 Arsenic hollow cathode lamp, or electrodeless discharge lamp (EDL): EDLs provide better sensitivity for arsenic analysis.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Data systems recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1,000 uL, as required.

5.0 REAGENTS

5.1 Reagent water: Water should be monitored for impurities. All references to water will refer to reagent water.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If a method blank using the acid is <MDL, the acid can be used.

5.3. Hydrogen peroxide (30%): Oxidant should be analyzed to determine levels of impurities. If a method blank using the H_2O_2 is <MDL, the reagent can be used.

5.4 Arsenic standard stock solution (1,000 mg/L): Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.320 g of arsenic trioxide (As_2O_3, analytical reagent grade) or equivalent in 100 mL of reagent water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 liter (1 mL = 1 mg As).

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ or equivalent in reagent water and dilute to 100 mL.

5.6 Nickel nitrate solution (1%): Dilute 20 mL of the 5% nickel nitrate to 100 mL with reagent water.

5.7 Arsenic working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add concentrated HNO_3, 30% H_2O_2, and 5% nickel nitrate solution or other appropriate matrix modifier. Amounts added should be representative of the concentrations found in the samples. Dilute to 100 mL with reagent water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile arsenic compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid and refrigerated prior to analysis.

6.5 Although waste samples do not need to be refrigerated sample handling and storage must comply with the minimum requirements established in Chapter One.

7.0 PROCEDURE

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Paragraphs 7.1.1-7.1.3. Sludge-type samples should be prepared according to Method 3050A. The applicability of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer a known volume of well-mixed sample to a 250-mL Griffin beaker or equivalent; add 2 mL of 30% H_2O_2 and sufficient concentrated HNO_3 to result in an acid concentration of 1% (v/v). Heat, until digestion is complete, at 95°C or until the volume is slightly less than 50 mL.

7.1.2 Cool, transfer to a volumetric flask, and bring back to 50 mL with reagent water.

7.1.3 Pipet 5 mL of this digested solution into a 10-mL volumetric flask, add 1 mL of the 1% nickel nitrate solution or other appropriate matrix modifier, and dilute to 10 mL with reagent water. The sample is now ready for injection into the furnace.

7.2 The 193.7-nm wavelength line and a background correction system are required. Follow the manufacturer's suggestions for all other spectrophotometer parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 206.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The optimal concentration range for aqueous samples using this method is 5-100 ug/L. Concentration ranges for non-aqueous samples will vary with matrix type.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

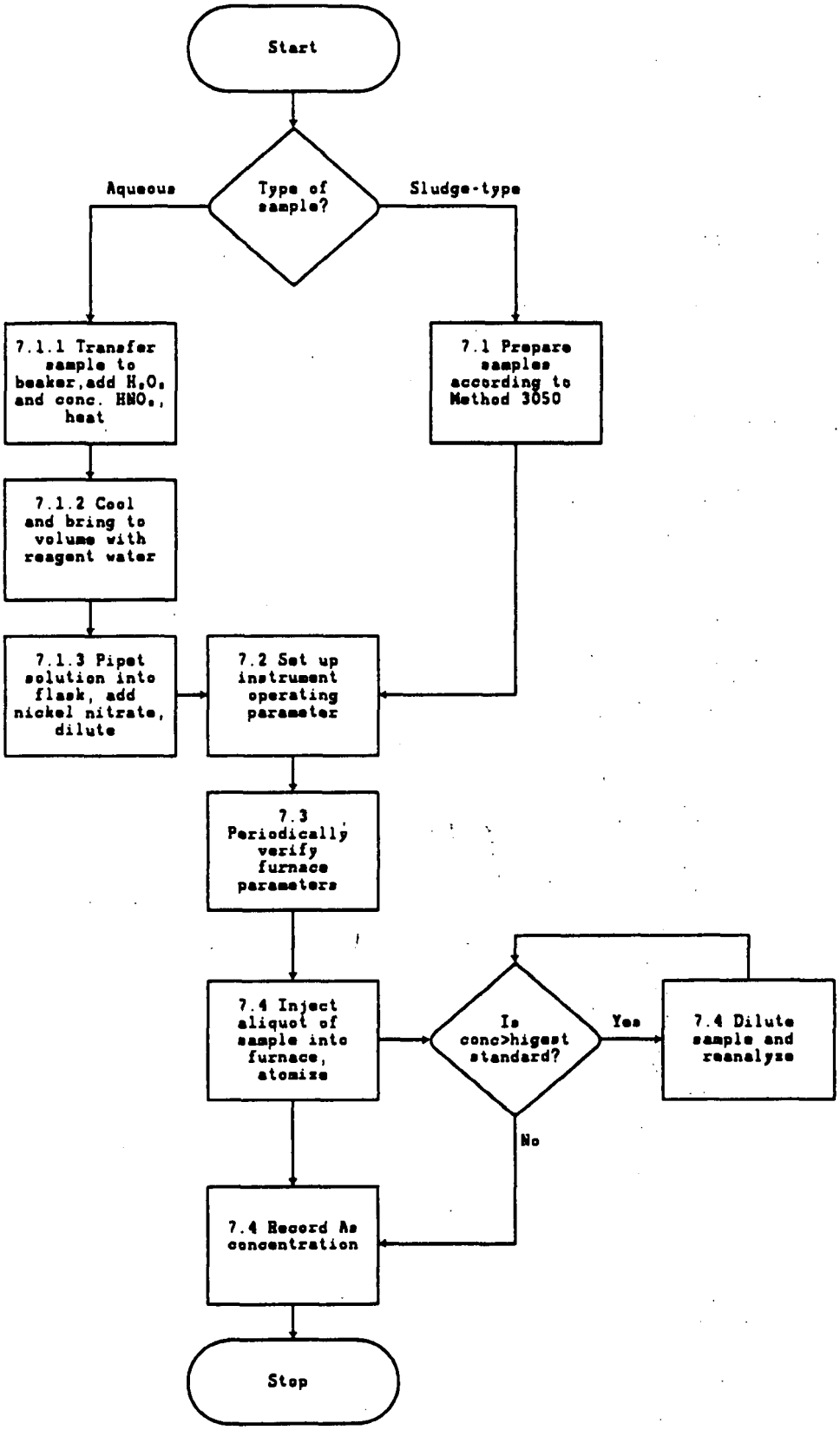
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.2.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Contaminated soil	3050	2.0, 1.8 ug/g
Oily soil	3050	3.3, 3.8 ug/g
NBS SRM 1646 Estuarine sediment	3050	8.1, 8.33 ug/g[a]
Emission control dust	3050	430, 350 ug/g

[a]Bias of -30 and -28% from expected, respectively.


Start
Type of sample?
Aqueous
Sludge-type
7.1.1 Transfer sample to beaker, add H_2O_2 and conc. HNO_3, heat
7.1 Prepare samples according to Method 3050
7.1.2 Cool and bring to volume with reagent water
7.1.3 Pipet solution into flask, add nickel nitrate, dilute
7.2 Set up instrument operating parameter
7.3 Periodically verify furnace parameters
7.4 Inject aliquot of sample into furnace, atomize
Is conc>higest standard?
Yes
7.4 Dilute sample and reanalyze
No
7.4 Record As concentration
Stop

7061A

METHOD 7061A

ARSENIC (ATOMIC ABSORPTION, GASEOUS HYDRIDE)

1.0 SCOPE AND APPLICATION

1.1 Method 7061 is an atomic absorption procedure for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and ground water. Method 7061A is approved only for sample matrices that do not contain high concentrations of chromium, copper, mercury, nickel, silver, cobalt, and molybdenum. All samples must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are employed to determine the applicability of the method to a given waste.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric/sulfuric acid digestion procedure described in this method (Step 7.1). Next, the arsenic in the digestate is reduced to the trivalent form with tin chloride. The trivalent arsenic is then converted to a volatile hydride using hydrogen produced from a zinc/hydrochloric acid reaction.

2.2 The volatile hydride is swept into an argon-hydrogen flame located in the optical path of an atomic absorption spectrophotometer. The resulting absorption of the lamp radiation is proportional to the arsenic concentration.

2.3 The typical detection limit for this method is 0.002 mg/L.

3.0 INTERFERENCES

3.1 High concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver can cause analytical interferences.

3.2 Traces of nitric acid left following the sample work-up can result in analytical interferences. Nitric acid must be distilled off by heating the sample until fumes of sulfur trioxide (SO_3) are observed.

3.3 Elemental arsenic and many of its compounds are volatile; therefore, certain samples may be subject to losses of arsenic during sample preparation.

4.0 APPARATUS AND MATERIALS

4.1 Beaker or equivalent - 100-mL.

4.2 Electric hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95°C.

4.3.1 Medicine dropper - Capable of fitting into a size "0" rubber stopper and delivering 1.5 mL.

4.3.2 Pear-shaped reaction flask - 50-mL, with two 14/20 necks (Scientific Glass JM-5835 or equivalent).

4.3.3 Gas inlet-outlet tube - Constructed from a micro cold-finger condenser (JM-3325) by cutting the portion below the 14/20 ground-glass joint.

4.3.4 Magnetic stirrer - To homogenize the zinc slurry.

4.3.5 Polyethylene drying tube - 10-cm, filled with glass to prevent particulate matter from entering the burner.

4.3.6 Flow meter - Capable of measuring 1 liter/min.

4.3.7 Class A volumetric flasks.

4.3.8 Graduated cylinder or equivalent.

4.4 Atomic absorption spectrophotometer - Single or dual channel, single- or double-beam instrument having a grating monochromator, photo-multiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip-chart recorder.

4.5 Burner - Recommended by the particular instrument manufacturer for the argon-hydrogen flame.

4.6 Arsenic hollow cathode lamp or arsenic electrodeless discharge lamp.

4.7 Strip-chart recorder.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water will be interferent free. All references to water in the method refer to reagent water unless otherwise specified.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine levels of impurities. If a method blank is < MDL, the acid can be used.

5.4 Sulfuric acid (concentrated), H_2SO_4. Acid should be analyzed to determine levels of impurities. If a method blank is < MDL, the acid can be used.

5.5 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine levels of impurities. If a method blank is < MDL, the acid can be used.

5.6 Diluent - Add 100 mL 18N H_2SO_4 and 400 mL concentrated HCl to 400 mL water and dilute to a final volume of 1 liter with water.

5.7 Potassium iodide solution - Dissolve 20 g KI in 100 mL water.

5.8 Stannous chloride solution - Dissolve 100 g $SnCl_2$ in 100 mL concentrated HCl.

5.9 Arsenic solutions

5.9.1 Arsenic standard solution (1,000 mg/L) - Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.320 g of arsenic trioxide As_2O_3 in 100 mL of water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 liter.

5.9.2 Intermediate arsenic solution - Pipet 1 mL stock arsenic solution into a 100-mL volumetric flask and bring to volume with water containing 1.5 mL concentrated HNO_3/liter (1 mL = 10 ug As).

5.9.3 Standard arsenic solution - Pipet 10 mL intermediate arsenic solution into a 100-mL volumetric flask and bring to volume with water containing 1.5 mL concentrated HNO_3/liter (1 mL = 1 ug As).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g. containers used for volatile organic analysis) may have to be used if very volatile arsenic compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of < 2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Place a 50-mL aliquot of digested sample (or, in the case of analysis of EP extracts, 50 mL) of the material to be analyzed in a 100-mL beaker. Add 10 mL concentrated HNO_3 and 12 mL 18N H_2SO_4. Evaporate the sample in the hood on an electric hot plate until white SO_3 fumes are observed (a volume of about 20 mL). Do not let the sample char. If charring occurs, immediately turn off the heat, cool, and add an additional 3 mL of HNO_3. Continue to add additional HNO_3 in order to maintain an excess (as evidenced by the formation of brown fumes). Do not let the solution darken, because arsenic may be reduced and lost. When the sample remains colorless or straw yellow during evolution of SO_3 fumes, the digestion is complete. Cool the sample, add about 25 mL water, and again evaporate until SO_3 fumes are produced in order to expel oxides of nitrogen. Cool. Transfer the digested sample to a 100-mL volumetric flask. Add 40 mL of concentrated HCl and bring to volume with water.

7.2 Prepare working standards from the standard arsenic solution. Transfer 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of standard to 100-mL volumetric flasks and bring to volume with diluent. These concentrations will be 0, 5, 10, 15, 20, and 25 ug As/liter.

7.3 If EP extracts are being analyzed or if a matrix interference is encountered, take the 15-, 20-, and 25-mg/liter standards and quantitatively transfer 25 mL of each of these standards into separate 50-mL volumetric flasks. Add 10 mL of the prepared sample to each flask. Bring to volume with water containing 1.5 mL HCl/liter.

7.4 Add 10 mL of prepared sample to a 50-mL volumetric flask. Bring to volume with water containing 1.5 mL HCl/liter. This is the zero addition aliquot.

NOTE: The absorbance from the zero addition aliquot will be one-fifth that produced by the prepared sample. The absorbance from the spiked samples will be one-half that produced by the standards plus the contribution from one-fifth of the prepared sample. Keeping these absorbances in mind will assist in judging the correct dilutions to produce optimum absorbance.

7.5 Transfer a 25-mL portion of the digested sample or standard to the reaction vessel and add 1 mL KI solution. Add 0.5 mL $SnCl_2$ solution. Allow at least 10 minutes for the metal to be reduced to its lowest oxidation state. Attach the reaction vessel to the special gas inlet-outlet glassware. Fill the medicine dropper with 1.50 mL zinc slurry that has been kept in suspension with the magnetic stirrer. Firmly insert the stopper containing the medicine dropper into the side neck of the reaction vessel. Squeeze the bulb to introduce the zinc slurry into the sample or standard solution. The metal hydride will produce a peak almost immediately. After the recorder pen begins to return to the base line, the reaction vessel can be removed.

CAUTION: Arsine is very toxic. Precautions must be taken to avoid inhaling arsine gas.

7.6 Use the 193.7-nm wavelength and background correction for the analysis of arsenic.

7.7 Follow the manufacturer's instructions for operating an argon-hydrogen flame. The argon-hydrogen flame is colorless; therefore, it may be useful to aspirate a low concentration of sodium to ensure that ignition has occurred.

7.8 If the method of standard additions was employed, plot the absorbances of spiked samples and blank vs. the concentrations. The extrapolated value will be one-fifth the concentration of the original sample. If the plot does not result in a straight line, a nonlinear interference is present. This problem can sometimes be overcome by dilution or addition of other reagents if there is some knowledge about the waste. If the method of standard additions was not required, then the concentration can be part of the calibration curve.

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 206.3 of Methods for Chemical Analysis of Water and Wastes.

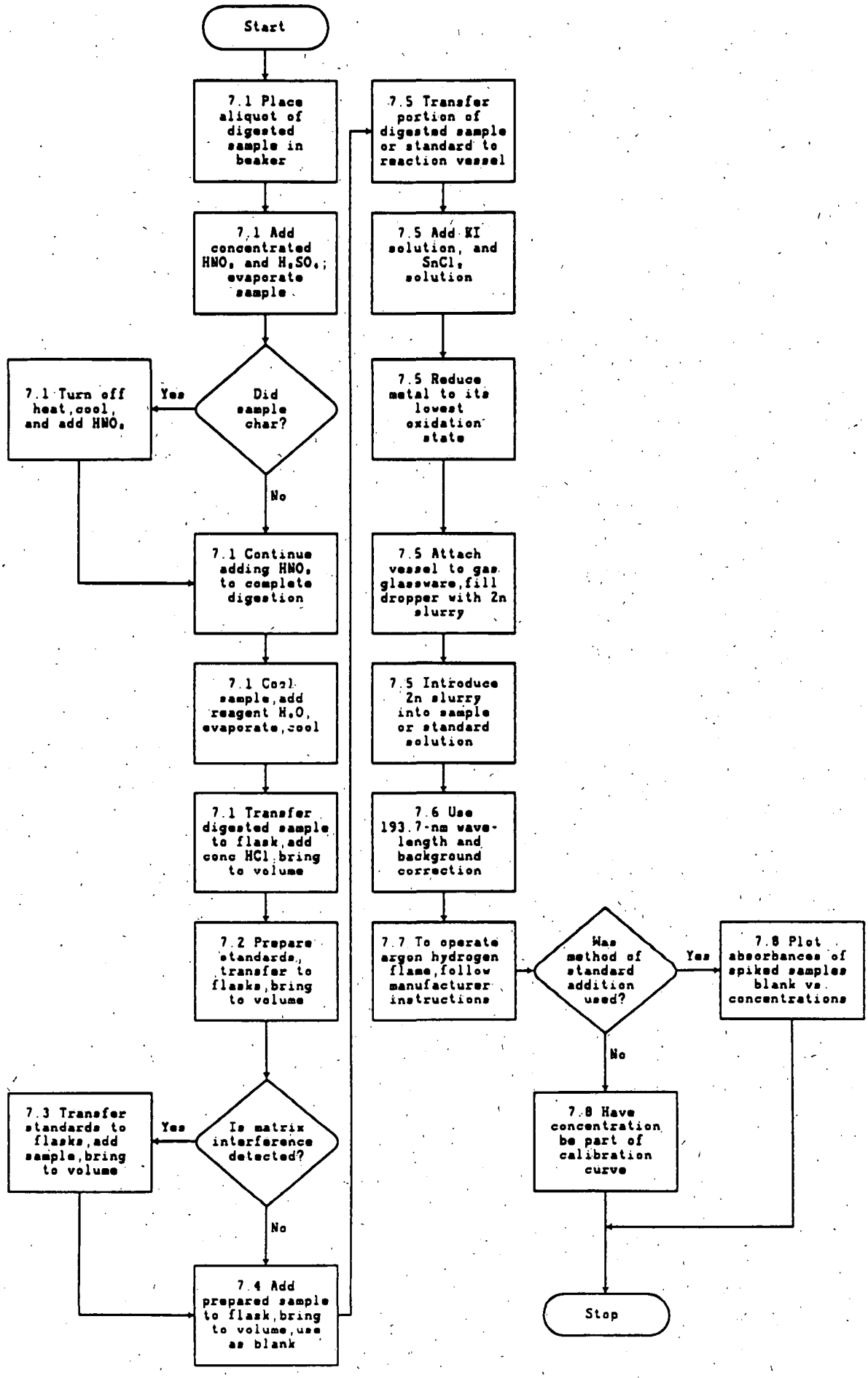
10.0 REFERENCES

1. Methods For Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.3.

2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

3. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

METHOD 7061A
ARSENIC (ATOMIC ABSORPTION, GASEOUS HYDRIDE)



METHOD 7062

ANTIMONY AND ARSENIC (ATOMIC ABSORPTION, BOROHYDRIDE REDUCTION)

1.0 SCOPE AND APPLICATION

1.1 Method 7062 is an atomic absorption procedure for determining 1 µg/L to 400 µg/L concentrations of antimony and arsenic in wastes, mobility procedure extracts, soils, and ground water. Method 7062 is approved for sample matrices that contain up to a total of 4000 mg/L concentrations of cobalt, copper, iron, mercury, or nickel. A solid sample can contain up to 40% by weight of the interferents before exceeding 4000 mg/L in a digested sample. All samples including aqueous matrices must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are used to determine the applicability of the method to a given waste.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric acid digestion procedure described in Method 3010 for aqueous and extract samples and the nitric/peroxide/hydrochloric acid digestion procedure described in Method 3050 (furnace AA option) for sediments, soils, and sludges. Excess peroxide is removed by evaporating samples to near dryness at the end of the digestion followed by degassing the samples upon addition of urea. L-cysteine is then added as a masking agent. Next, the antimony and arsenic in the digest are reduced to the trivalent forms with potassium iodide. The trivalent antimony and arsenic are then converted to volatile hydrides using hydrogen produced from the reaction of the acidified sample with sodium borohydride in a continuous-flow hydride generator.

2.2 The volatile hydrides are swept into, and decompose in, a heated quartz cell located in the optical path of an atomic absorption spectrophotometer. The resulting absorption of the lamp radiation is proportional to the arsenic or antimony concentration.

2.3 The typical detection limit for this method is 1.0 µg/L.

3.0 INTERFERENCES

3.1 Very high (>4000 mg/L) concentrations of cobalt, copper, iron, mercury, and nickel can cause analytical interferences through precipitation as reduced metals and associated blockage of transfer lines and fittings.

3.2 Traces of peroxides left following the sample work-up can result in analytical interferences. Peroxides must be removed by evaporating each sample to near dryness followed by reaction with urea and allowing sufficient time for degassing before analysis (see Sections 7.1 and 7.2).

3.3 Even after acid digestion, organic compounds will remain in the sample. These flame gases and these organic compounds can absorb at the analytical wavelengths and background correction must be used.

4.0 APPARATUS AND MATERIALS

4.1 Electric hot plate: Large enough to hold at least several 100 mL Pyrex digestion beakers.

4.2 A continuous-flow hydride generator: A commercially available continuous-flow sodium borohydride/HCl hydride generator or a generator constructed similarly to that shown in Figure 1 (P. S. Analytical or equivalent).

4.2.1 Peristaltic Pump: A four-channel, variable-speed peristaltic pump to permit regulation of liquid-stream flow rates (Ismatec Reglo-100 or equivalent). Pump speed and tubing diameters should be adjusted to provide the following flow rates: sample/blank flow = 4.2 mL/min; borohydride flow = 2.1 mL/min; and potassium iodide flow = 0.5 mL/min.

4.2.2 Sampling Valve (optional): A sampling valve (found in the P. S. Analytical Hydride Generation System or equivalent) that allows switching between samples and blanks (rinse solution) without introduction of air into the system will provide more signal stability.

4.2.3 Transfer Tubing and Connectors: Transfer tubing (1 mm I.D.), mixing T's, and connectors are made of a fluorocarbon (PFA or TFM) and are of compatible sizes to form tight, leak-proof connections (Latchat, Technicon, etc. flow injection apparatus accessories or equivalent).

4.2.4 Mixing Coil: A 20-turn coil made by wrapping transfer tubing around a 1-cm diameter by 5-cm long plastic or glass rod (see Figure 1).

4.2.5 Mixing Coil Heater, if appropriate: A 250-mL Erlenmeyer flask containing 100 mL of water heated to boiling on a dedicated one-beaker hotplate (Corning PC-35 or equivalent). The mixing coil in 4.2.4 is immersed in the boiling water to speed kinetics of the hydride forming reactions and increase solubility of interfering reduced metal precipitates.

4.2.6 Gas-Liquid Separator: A glass apparatus for collecting and separating liquid and gaseous products (P.T. Analytical accessory or equivalent) which allows the liquid fraction to drain to waste and gaseous products above the liquid to be swept by a regulated carrier gas (argon) out of the cell for analysis. To avoid undue carrier gas dilution, the gas volume above the liquid should not exceed 20 mL. See Figure 1 for an acceptable separator shape.

4.2.7 Condensor: Moisture picked up by the carrier gas must be removed before encountering the hot absorbance cell. The moist carrier gas with the hydrides is dried by passing the gasses through a small (< 25

mL) volume condensor coil (Ace Glass Model 6020-02 or equivalent) that is cooled to 5°C by a water chiller (Neslab RTE-110 or equivalent). Cool tap-water in place of a chiller is acceptable.

4.2.8 Flow Meter/Regulator: A meter capable of regulating up to 1 L/min of argon carrier gas is recommended.

4.3 Absorbance Cell: A 17 cm or longer quartz tube T-cell (windowless is strongly suggested) is recommended, as shown in Figure 1 (Varian Model VGA-76 accessory or equivalent). The cell is held in place by a holder that positions the cell about 1 cm over a conventional AA air-acetylene burner head. In operation, the cell is heated to around 900°C.

4.4 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with an appropriate recording device.

4.5 Burner: As recommended by the particular instrument manufacturer for an air-acetylene flame. An appropriate mounting bracket attached to the burner that suspends the quartz absorbance cell between 1 and 2 cm above the burner slot is required.

4.6 Antimony and arsenic hollow cathode lamps or antimony and arsenic electrodeless discharge lamps and power supply. Super-charged hollow-cathode lamps or EDL lamps are recommended for maximum sensitivity.

4.7 Strip-chart recorder (optional): Connect to output of spectrophotometer.

5.0 REAGENTS

5.1 Reagent water: Water must be monitored for impurities. Refer to Chapter 1 for definition of Reagent water.

5.2 Concentrated nitric acid (HNO_3): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.3 30% Hydrogen peroxide (H_2O_2): Peroxide must be a tin-free grade.

5.4 Concentrated hydrochloric acid (HCl): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.5 Diluent solution: A 3% HCl solution in reagent water must be prepared as a diluent solution if excessive levels of analytes or interfering metals are found in the undiluted samples.

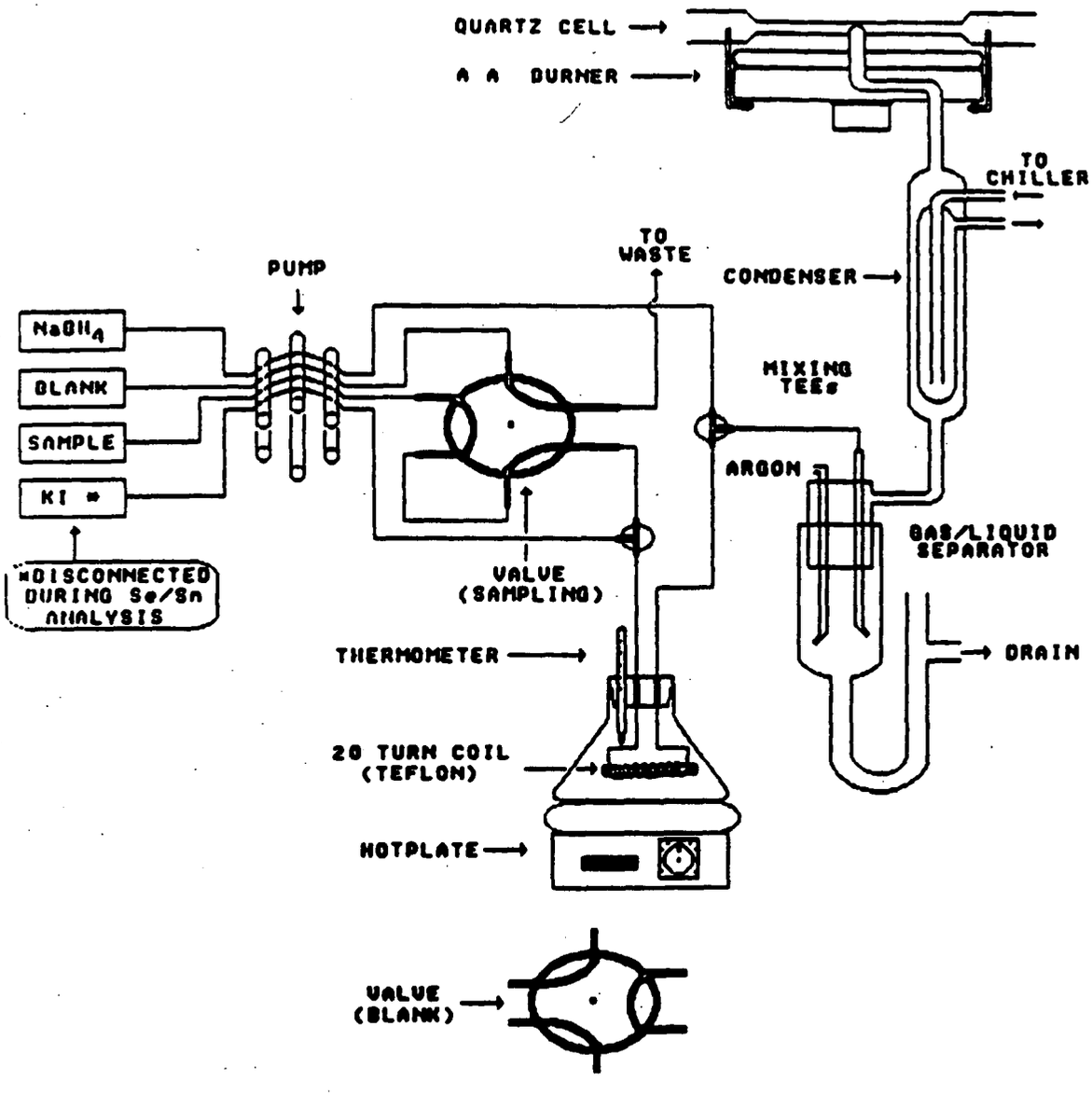


Figure 1. Continuous-flow sodium borohydride/hydride generator apparatus set-up and an AAS sample introduction system.

5.6 Urea (H_2NCONH_2): A 5.00-g portion of reagent grade urea must be added to a 25-mL aliquot of each sample for removal of excess peroxide through degassing (see Section 7.2).

5.7 L-cysteine ($C_6H_{12}N_2O_4S_2$): A 1.00-g portion of reagent grade L-cystine must be added to a 25-mL aliquot of each sample for masking the effects of suppressing transition metals (see Section 7.2).

5.8 20% Potassium iodide (KI): A 20% KI solution (20 g reagent-grade KI dissolved and brought to volume in 100 mL reagent water) must be prepared for reduction of antimony and arsenic to their +3 valence states.

5.9 4% Sodium borohydride ($NaBH_4$): A 4% sodium borohydride solution (20 g reagent-grade $NaBH_4$ plus 2 g sodium hydroxide dissolved in 500 mL of reagent water) must be prepared for conversion of the antimony and arsenic to their hydrides.

5.10 Analyte solutions:

5.10.1 **Antimony and arsenic stock standard solution** (1,000 mg/L): Either procure certified aqueous standards from a supplier and verify by comparison with a second standard, or dissolve 1.197 g of antimony trioxide Sb_2O_3 and 1.320 g of arsenic trioxide As_2O_3 in 100 mL of reagent water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 liter.

5.10.2 **Intermediate antimony and arsenic solution:** Pipet 1 mL stock antimony and arsenic solution into a 100-mL volumetric flask and bring to volume with reagent water containing 1.5 mL concentrated HNO_3/liter (1 mL = 10 μg each of Sb and As).

5.10.3 **Standard antimony and arsenic solution:** Pipet 10 mL intermediate antimony and arsenic solution into a 100-mL volumetric flask and bring to volume with reagent water containing 1.5 mL concentrated HNO_3/liter (1 mL = 1 μg each of Sb and As).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile antimony and arsenic compounds are suspected to be present in the samples.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Place a 100-mL portion of an aqueous sample or extract or 1.000 g of a dried solid sample in a 250-mL digestion beaker. Digest aqueous samples and extracts according to Method 3010. Digest solid samples according to Method 3050 (furnace AA option) with the following modifications: add 5 mL of concentrated hydrochloric acid just prior to the final volume reduction stage to aid in antimony recovery; the final volume reduction should be to less than 5 mL but not to dryness to adequately remove excess hydrogen peroxide (see note). After dilution to volume, further dilution with diluent may be necessary if analytes are known to exceed 400 µg/L or if interferents are expected to exceed 4000 mg/L in the digestate.

> Note: For solid digestions, the volume reduction stage is critical to obtain accurate data, especially for arsenic. Close monitoring of each sample is necessary when this critical stage is reached.

7.2 Prepare samples for hydride analysis by adding 5.00 g urea, 1.00 g L-cysteine, and 20 mL concentrated HCl to a 25-mL aliquot of digested sample in a 50-mL volumetric flask. Heat in a water bath until the L-cysteine has dissolved and effervescence has subsided (At least 30 minutes is suggested. If effervescense is still seen, repeat step 7.1 with more volume reduction.). Bring flask to volume with reagent water before analyzing. A 1:1 dilution correction must be made in the final concentration calculations.

7.3 Prepare working standards from the standard antimony and arsenic solution. Transfer 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of standard to 100-mL volumetric flasks and bring to volume with diluent. These concentrations will be 0, 5, 10, 15, 20, and 25 µg Sb and As/liter.

7.4 If EP extracts (Method 1310) are being analyzed for arsenic, the method of standard additions must be used. Spike appropriate amounts of intermediate or standard antimony and arsenic solution to three 25 mL aliquots of each unknown. Spiking volumes should be kept less than 0.250 mL to avoid excessive spiking dilution errors.

7.5 Set up instrumentation and hydride generation apparatus and fill reagent containers. The sample and blank flows should be set around 4.2 mL/min, the borohydride flow around 2.1 mL/min, and the potassium iodide flow around 0.5 mL/min. The argon carrier gas flow is adjusted to about 200 mL/min. For the AA, use the 217.6-nm wavelength and 0.7-nm slit width (or manufacturer's recommended slit-width) without background correction if analyzing for antimony. Use the 193.7-nm wavelength and 0.7-nm slit width (or manufacturer's recommended slit-width) with background correction for the analysis of arsenic. Begin all flows and allow 10 minutes for warm-up.

7.6 Place sample feed line into a prepared sample solution and start pump to begin hydride generation. Wait for a maximum steady-state signal on the strip-chart recorder or output meter. Switch to blank sample and watch for signal to decline to baseline before switching to the next sample and beginning the next analysis. Run standards first (low to high), then unknowns. Include appropriate QA/QC solutions, as required. Prepare calibration curves and convert absorbances to concentration. If a heating coil is not being used, KI must be added to the samples and heated for thirty minutes to ensure reduction.

CAUTION: The hydrides of antimony and arsenic are very toxic. Precautions must be taken to avoid inhaling the gas.

7.7 If the method of standard additions was employed, plot the measured concentration of the spiked samples and unspiked sample versus the spiked concentrations. The spiked concentration axis intercept will be the method of standard additions concentration. If the plot does not result in a straight line, a nonlinear interference is present. This problem can sometimes be overcome by dilution or addition of other reagents if there is some knowledge about the waste. If the method of standard additions was not required, then the concentration is determined from a standard calibration curve.

8.0 QUALITY CONTROL

8.1 See section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

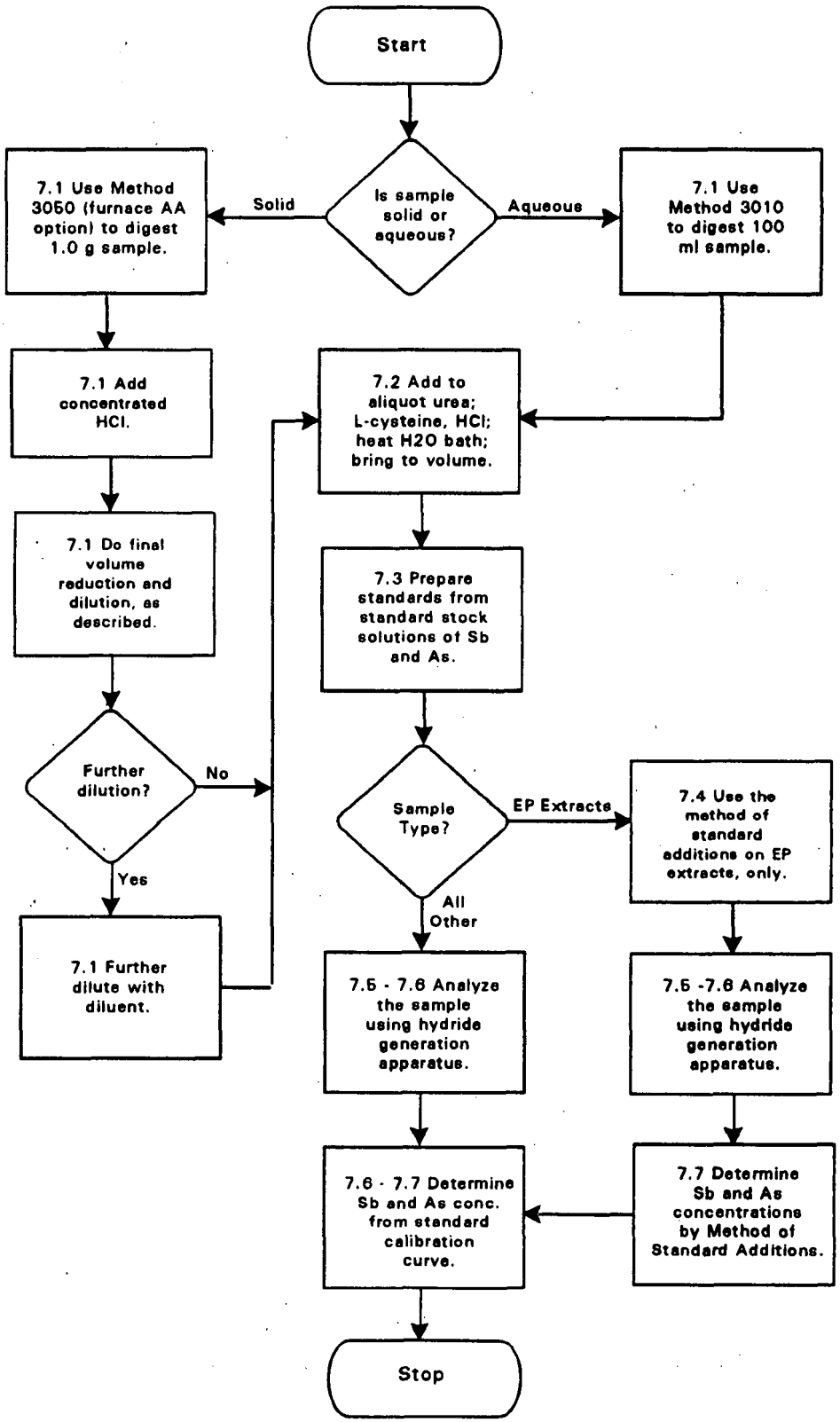
9.1 The relative standard deviations obtained by a single laboratory for 7 replicates of a contaminated soil were 18% for antimony at 9.1 ug/L in solution and 4.6% for arsenic at 68 ug/L in solution. The average percent recovery of the analysis of an 8 μg/L spike on ten different samples is 103.7% for arsenic and 95.6% for antimony.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.3.

2. "Evaluation of Hydride Atomic Absorption Methods for Antimony, Arsenic, Selenium, and Tin", an EMSL-LV internal report under Contract 68-03-3249, Job Order 70.16, prepared for T. A. Hinners by D. E. Dobb, and J. D. Lindner of Lockheed Engineering and Sciences Co., and L. V. Beach of the Varian Corporation.

METHOD 7062
ANTIMONY AND ARSENIC (ATOMIC ABSORPTION, BOROHYDRIDE REDUCTION)



METHOD 7080

BARIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 High hollow cathode current settings and a narrow spectral band pass must be used, because both barium and calcium emit strongly at barium's analytical wavelength.

3.3 Barium undergoes significant ionization in the nitrous oxide/acetylene flame, resulting in a significant decrease in sensitivity. All samples and standards must contain 2 mL of the KCl ionization suppressant (Section 5.2.3 below) per 100 mL of solution.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Barium hollow cathode lamp.
4.2.2 Wavelength: 553.6 nm.
4.2.3 Fuel: Acetylene.
4.2.4 Oxidant: Nitrous oxide.
4.2.5 Type of flame: Fuel rich.
4.2.6 Background correction: Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.7787 g barium chloride ($BaCl_2 \cdot 2H_2O$, analytical reagent grade in Type II water and dilute to

1 liter. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing. All calibration standards and samples should contain 2 mL/100 mL of the potassium chloride (ionization suppressant) solution described in Section 5.2.3.

5.2.3 **Potassium chloride solution:** Dissolve 95 g potassium chloride (KCl) in Type II water and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

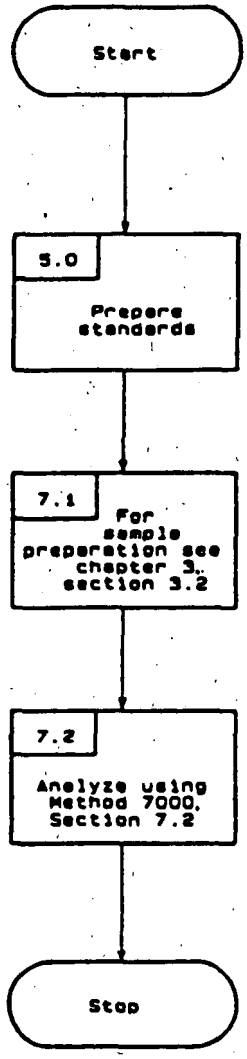
9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 1-20 mg/L with a wavelength of 553.6 nm.
Sensitivity: 0.4 mg/L.
Detection limit: 0.1 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 0.4 and 2 mg Ba/L gave standard deviations of ±0.043 and ±0.13, respectively. Recoveries at these levels were 94% and 113%, respectively.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 208.1.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5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7080A

BARIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 High hollow cathode current settings and a narrow spectral band pass must be used, because both barium and calcium emit strongly at barium's analytical wavelength.

3.3 Barium undergoes significant ionization in the nitrous oxide/acetylene flame, resulting in a significant decrease in sensitivity. All samples and standards must contain a ionization suppressant. The type of suppressant and concentration used must be documented.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Barium hollow cathode lamp.
4.2.2 Wavelength: 553.6 nm.
4.2.3 Fuel: Acetylene.
4.2.4 Oxidant: Nitrous oxide.
4.2.5 Type of flame: Fuel rich.
4.2.6 Background correction: Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.7787 g barium chloride ($BaCl_2 \cdot 2H_2O$) analytical reagent grade in reagent water and dilute to 1 liter (1000 mg/L). Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards

should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing. All calibration standards and samples should contain the ionization suppressant.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Section 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

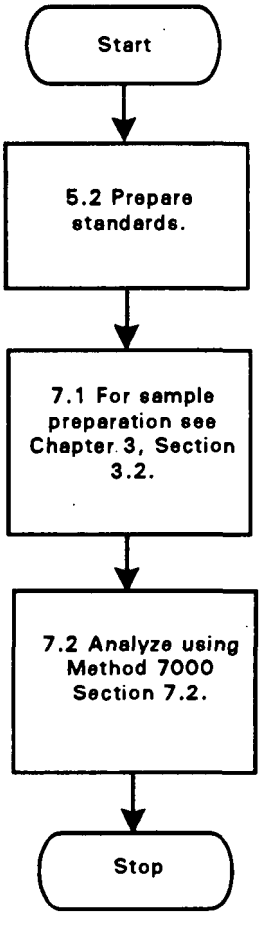
9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 1-20 mg/L with a wavelength of 553.6 nm.
Sensitivity: 0.4 mg/L.
Detection limit: 0.1 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 0.4 and 2 mg Ba/L gave standard deviations of ±0.043 and ±0.13, respectively. Recoveries at these levels were 94% and 113%, respectively.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 208.1.


Start
5.2 Prepare standards.
7.1 For sample preparation see Chapter 3, Section 3.2.
7.2 Analyze using Method 7000 Section 7.2.
Stop

7081

METHOD 7081

BARIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000.

3.2 Barium is known to form a barium carbide in the graphite furnace. This less volatile carbide can cause losses of sensitivity and memory effects.

3.3 The long residence time and the high concentration of the analyte in the optical path of the graphite furnace can lead to severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.4 Because of possible chemical interaction, nitrogen should not be used as a purge gas.

3.5 Halide acids should not be used.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Drying time and temp: 30 sec at 125°C.

4.2.2 Ashing time and temp: 30 sec at 1200°C.

4.2.3 Atomizing time and temp: 10 sec at 2800°C.

4.2.4 Purge gas: Argon (nitrogen should <u>not</u> be used).

4.2.5 Wavelength: 553.6 nm.

4.2.6 Background correction: Not required.

4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards

5.2.1 Stock solution - Dissolve 1.7787 g barium chloride ($BaCl_2$ $2H_2O$, analytical reagent grade) in water and dilute to 1 liter. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Step 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample Preparation - The procedures for preparation of the sample are given in Chapter Three, Step 3.2.

7.2 See Method 7000, Step 7.3, Furnace Technique.

8.0 QUALITY ASSURANCE

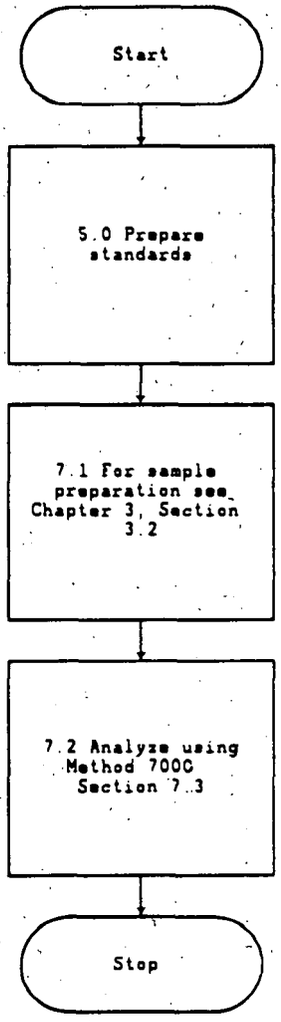
8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are not available at this time.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.


Start
5.0 Prepare standards
7.1 For sample preparation see Chapter 3, Section 3.2
7.2 Analyze using Method 7000C Section 7.3
Stop

METHOD 7131

CADMIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, cadmium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction is required to avoid erroneously high results.

3.3 Excess chloride may cause premature volatilization of cadmium. Ammonium phosphate used as a matrix modifier minimizes this loss.

3.4 Many plastic pipet tips (yellow) contain cadmium. Use "cadmium-free" tips.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Drying time and temp:** 30 sec at 125°C.
4.2.2 **Ashing time and temp:** 30 sec at 500°C.
4.2.3 **Atomizing time and temp:** 10 sec at 1900°C.
4.2.4 **Purge gas:** Argon.
4.2.5 **Wavelength:** 228.8 nm.
4.2.6 **Background correction:** Required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g of cadmium metal (analytical reagent grade) in 20 mL of 1:1 HNO_3 and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock cadmium solution to be used as **calibration standards** at the time of analysis. To each 100 mL of standard and sample alike add 2.0 mL of the ammonium phosphate solution. The calibration standards should be prepared to contain 0.5% (v/v) HNO_3.

5.2.3 **Ammonium phosphate solution** (40%): Dissolve 40 g of ammonium phosphate, $(NH_4)_2HPO_4$ (analytical reagent grade), in Type II water and dilute to 100 mL.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 213.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.5-10 ug/L.
Detection limit: 0.1 ug/L.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

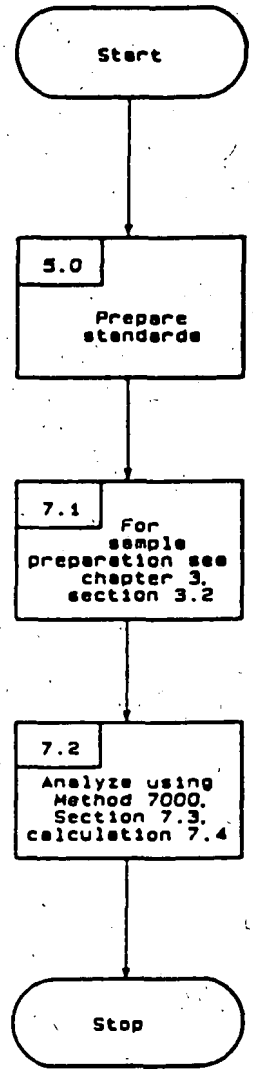
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 213.2.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Lagoon soil	3050	0.10, 0.095 ug/g
NBS SRM 1646 Estuarine sediment	3050	0.35 ug/g[a]
Solvent extract of oily waste	3030	1.39, 1.09 ug/L

[a]Bias of -3% from expected value.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.3, calculation 7.4
Stop

METHOD 7131A

CADMIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, cadmium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction is required to avoid erroneously high results.

3.3 Excess chloride may cause premature volatilization of cadmium. Ammonium phosphate used as a matrix modifier minimizes this loss. Other modifiers may be used as long as it is documented with the type of suppressant and concentration.

3.4 Many plastic pipet tips (yellow) contain cadmium. Use "cadmium-free" tips.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Drying time and temp: 30 sec at 125°C.

4.2.2 Ashing time and temp: 30 sec at 500°C.

4.2.3 Atomizing time and temp: 10 sec at 1900°C.

4.2.4 Purge gas: Argon.

4.2.5 Wavelength: 228.8 nm.

4.2.6 Background correction: Required.

4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.000 g of cadmium metal (analytical reagent grade) in 20 mL of 1:1 HNO_3 and dilute to 1 liter with reagent water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock cadmium solution to be used as calibration standards at the time of analysis. To each 100 mL of standard and sample alike add 2.0 mL of the ammonium phosphate solution. The calibration standards should be prepared to contain 0.5% (v/v) HNO_3.

5.2.3 Ammonium phosphate solution (40%): Dissolve 40 g of ammonium phosphate, $(NH_4)_2HPO_4$ (analytical reagent grade), in reagent water and dilute to 100 mL.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are provided in Chapter Three, Section 3.2.

7.2 See Method 7000, Section 7.3, Furnace Procedure. The calculation is provided in Method 7000, Section 7.4.

8.0 QUALITY CONTROL

8.1 Refer to Section 8.0 of Method 7000 .

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 213.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.5-10 ug/L.
Detection limit: 0.1 ug/L.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 213.2.

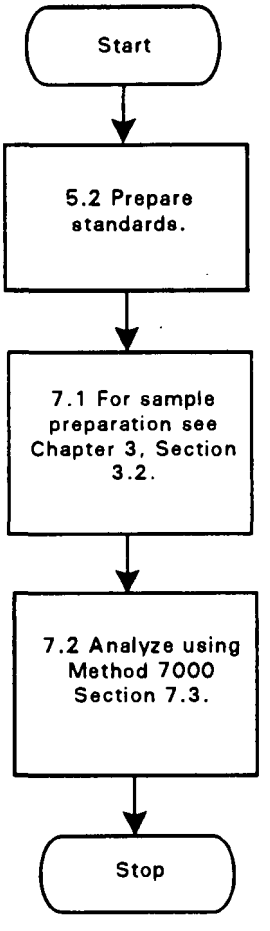
2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Lagoon soil	3050	0.10, 0.095 ug/g
NBS SRM 1646 Estuarine sediment	3050	0.35 ug/g[a]
Solvent extract of oily waste	3030	1.39, 1.09 ug/L

[a]Bias of -3% from expected value.

METHOD 7131A
CADMIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)



METHOD 7196A

CHROMIUM, HEXAVALENT (COLORIMETRIC)

1.0 SCOPE AND APPLICATION

1.1 Method 7196 is used to determine the concentration of dissolved hexavalent chromium [Cr(VI)] in EP/TCLP characteristic extracts and ground waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present (see Paragraph 3.1 below).

1.2 Method 7196 may be used to analyze samples containing from 0.5 to 50 mg of Cr(VI) per liter.

2.0 SUMMARY OF METHOD

2.1 Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, may be determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red-violet color of unknown composition is produced. The reaction is very sensitive, the absorbancy index per gram atom of chromium being about 40,000 at 540 nm. Addition of an excess of diphenylcarbazide yields the red-violet product, and its absorbance is measured photometrically at 540 nm.

3.0 INTERFERENCES

3.1 The chromium reaction with diphenylcarbazide is usually free from interferences. However, certain substances may interfere if the chromium concentration is relatively low. Hexavalent molybdenum and mercury salts also react to form color with the reagent; however, the red-violet intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200 mg/L of molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to 10 times that of chromium will not cause trouble.

3.2 Iron in concentrations greater than 1 mg/L may produce a yellow color, but the ferric iron color is not strong and difficulty is not normally encountered if the absorbance is measured photometrically at the appropriate wavelength.

4.0 APPARATUS AND MATERIALS

4.1 Colorimetric equipment: One of the following is required: Either a spectrophotometer, for use at 540 nm, providing a light path of 1 cm or longer, or a filter photometer, providing a light path of 1 cm or longer and equipped with a greenish-yellow filter having maximum transmittance near 540 nm.

5.0 REAGENTS

5.1 Reagent water: Reagent water should be monitored for impurities.

5.2 Potassium dichromate stock solution: Dissolve 141.4 mg of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in reagent water and dilute to 1 liter (1 mL = 50 ug Cr).

5.3 Potassium dichromate standard solution: Dilute 10.00 mL potassium dichromate stock solution to 100 mL (1 mL = 5 ug Cr).

5.4 Sulfuric acid, 10% (v/v): Dilute 10 mL of distilled reagent grade or spectrograde quality sulfuric acid, H_2SO_4, to 100 mL with reagent water.

5.5 Diphenylcarbazide solution: Dissolve 250 mg 1,5-diphenylcarbazide in 50 mL acetone. Store in a brown bottle. Discard when the solution becomes discolored.

5.6 Acetone (analytical reagent grade): Avoid or redistill material that comes in containers with metal or metal-lined caps.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Since the stability of Cr(VI) in extracts is not completely understood at this time, the analysis should be carried out as soon as possible.

6.3 To retard the chemical activity of hexavalent chromium, the samples and extracts should be stored at 4°C until analyzed. The maximum holding time prior to analysis of the samples or extracts is 24 hr. The 24 hr holding time begins after extraction.

7.0 PROCEDURE

7.1 Color development and measurement: Transfer 95 mL of the extract to be tested to a 100-mL volumetric flask. Add 2.0 mL diphenylcarbazide solution and mix. Add H_2SO_4 solution to give a pH of 2 $\pm$ 0.5, dilute to 100 mL with reagent water, and let stand 5 to 10 min for full color development. Transfer an appropriate portion of the solution to a 1-cm absorption cell and measure its absorbance at 540 nm. Use reagent water as a reference. Correct the absorbance reading of the sample by subtracting the absorbance of a blank carried through the method (see Note below). An aliquot of the sample containing all reagents except diphenylcarbazide should be prepared and used to correct the sample for turbidity (i.e., a turbidity blank). From the corrected absorbance, determine the mg/L of chromium present by reference to the calibration curve.

NOTE: If the solution is turbid after dilution to 100 mL in Step 7.1, above, take an absorbance reading before adding the carbazide

reagent and correct the absorbance reading of the final colored solution by subtracting the absorbance measured previously.

7.2 Preparation of calibration curve:

7.2.1 To compensate for possible slight losses of chromium during digestion or other operations of the analysis, treat the chromium standards by the same procedure as the sample. Accordingly, pipet a chromium standard solution in measured volumes into 250-mL beakers or conical flasks to generate standard concentrations ranging from 0.5 to 5 mg/L Cr(VI) when diluted to the appropriate volume.

7.2.2 Develop the color of the standards as for the samples. Transfer a suitable portion of each colored solution to a 1-cm absorption cell and measure the absorbance at 540 nm. As reference, use reagent water. Correct the absorbance readings of the standards by subtracting the absorbance of a reagent blank carried through the method. Construct a calibration curve by plotting corrected absorbance values against mg/L of Cr(VI).

7.3 Verification:

7.3.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting color development. This must be accomplished by analyzing a second 10-mL aliquot of the pH-adjusted filtrate that has been spiked with Cr(VI). The amount of spike added should double the concentration found in the original aliquot. Under no circumstances should the increase be less than 30 μg Cr(VI)/liter. To verify the absence of an interference, the spike recovery must be between 85% and 115%.

7.3.2 If addition of the spike extends the concentration beyond the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

7.3.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

7.3.4 If the interference persists after sample dilution, an alternative method (Method 7195, Coprecipitation, or Method 7197, Chelation/Extraction) should be used.

7.4 Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be performed by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/L Cr(VI), one can conclude that the analytical method has been verified.

7.5 Analyze all extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions (see Method 7000, Section 8.7).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection. Refer to Chapter One for more information.

8.2 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.3 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.4 Verify calibration with an independently prepared check standard every 15 samples.

8.5 Run one matrix spike replicate or one replicate sample for every ten samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process. Refer to Chapter One for more information concerning matrix spikes and matrix spike duplicates.

8.6 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

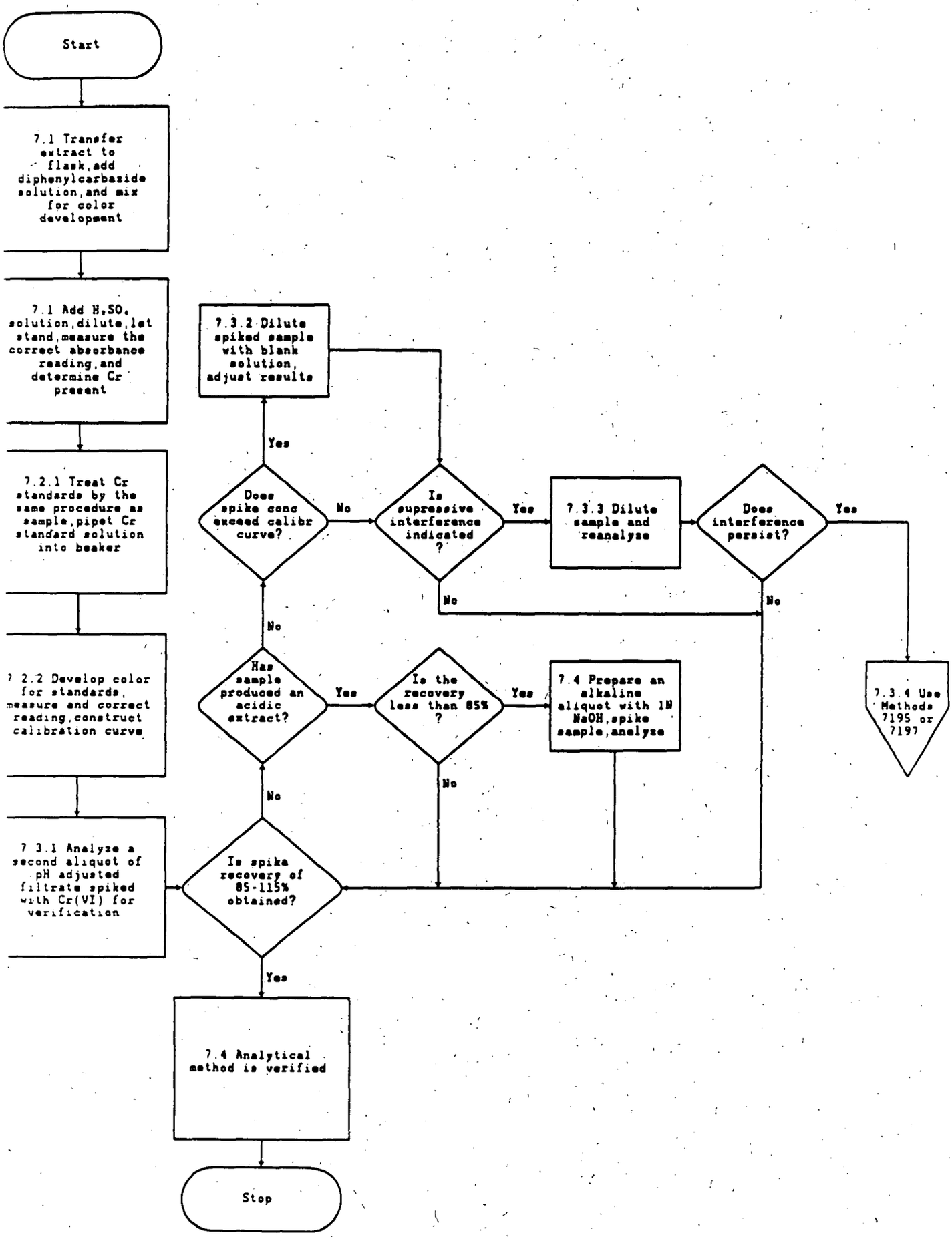
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Methods 218.4 and 218.5.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	Not known	0.096, 0.107 ug/g
Sediment from chemical storage area	3060	115, 117 ug/g


Start
7.1 Transfer extract to flask, add diphenylcarbazide solution, and mix for color development
7.1 Add H_2SO_4 solution, dilute, let stand, measure the correct absorbance reading, and determine Cr present
7.2.1 Treat Cr standards by the same procedure as sample, pipet Cr standard solution into beaker
7.2.2 Develop color for standards, measure and correct reading, construct calibration curve
7.3.1 Analyze a second aliquot of pH adjusted filtrate spiked with Cr(VI) for verification
Is spike recovery of 85-115% obtained?
Yes
No
Has sample produced an acidic extract?
Yes
No
Does spike conc exceed calibr curve?
Yes
No
7.3.2 Dilute spiked sample with blank solution, adjust results
Is supressive interference indicated ?
Yes
No
7.3.3 Dilute sample and reanalyze
Does interference persist?
Yes
No
7.3.4 Use Methods 7195 or 7197
Is the recovery less than 85% ?
Yes
No
7.4 Prepare an alkaline aliquot with 1N NaOH, spike sample, analyze
7.4 Analytical method is verified
Stop

METHOD 7211

COPPER (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 If interferences are suspected, see Section 3.0 of Method 7000.

3.2 Background correction may be required since nonspecific absorption and scattering can be significant at the analytical wavelength. Background correction with certain instruments may be difficult at this wavelength due to low intensity output from hydrogen or deuterium lamps. Consult specific instrument manufacturer's literature for details.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Drying time and temp: 30 sec at 125°C.

4.2.2 Ashing time and temp: 30 sec at 900°C.

4.2.3 Atomizing time and temp: 10 sec at 2700°C.

4.2.4 Purge gas: Argon or nitrogen.

4.2.5 Wavelength: 324.7 nm.

4.2.6 Background correction: Recommended.

4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards

5.2.1 Stock solution - Dissolve 1.00 g of electrolytic copper (analytical regent grade) in 5 mL redistilled HNO_3 and dilute to 1 liter with water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample to be analyzed after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Step 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample Preparation - The procedures for preparation of the sample are given in Chapter Three, Step 3.2.

7.2 See Method 7000, Step 7.3, Furnace Technique.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are not available at this time.

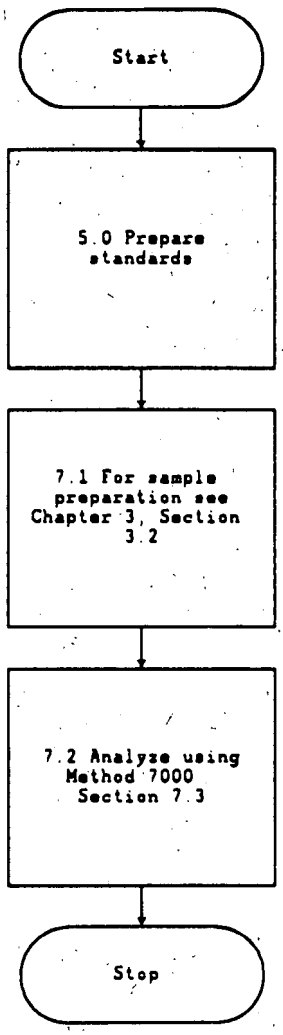
9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 5-100 ug/L.
Detection limit: 1 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.

METHOD 7211
COPPER (ATOMIC ABSORPTION, FURNACE TECHNIQUE)



METHOD 7381

IRON (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000.

3.2 Iron is a universal contaminant, particularly at the low levels determined by this method. Great care should be taken to avoid contamination.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Drying time and temp: 30 sec at 125°C.

4.2.2 Ashing time and temp: 30 sec at 1000°C.

4.2.3 Atomizing time and temp: 10 sec at 2700°C.

4.2.4 Purge gas: Argon or nitrogen.

4.2.5 Wavelength: 248.3 nm.

4.2.6 Background Correction: Recommended.

4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards

5.2.1 Stock solution - Dissolve 1.000 g iron wire (analytical reagent grade) in 10 mL redistilled HNO_3 and water and dilute to 1 liter with water. Note that iron passivates in concentrated HNO_3 and, thus, some water should be present. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample to be analyzed after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 See Chapter Three, Step 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation - The procedures for preparation of the sample are given in Chapter Three, Step 3.2.

7.2 See Method 7000, Step 7.3, Furnace Technique.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

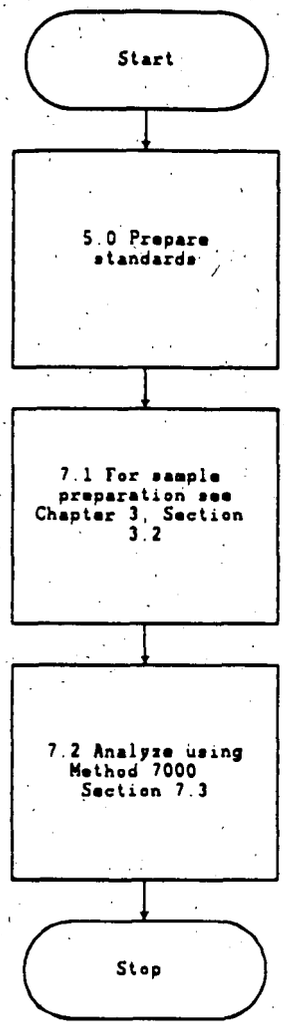
9.1 Precision and accuracy data are not available at this time.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 5-100 ug/L.
Detection limit: 1 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.


Start
5.0 Prepare standards
7.1 For sample preparation see Chapter 3, Section 3.2
7.2 Analyze using Method 7000 Section 7.3
Stop

METHOD 7430

LITHIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Lithium hollow cathode lamp.

4.2.2 Wavelength: 670.8 nm.

4.2.3 Fuel: Acetylene.

4.2.4 Oxidant: Air.

4.2.5 Type of flame: Oxidizing (fuel lean).

4.2.6 Background Correction: Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards

5.2.1 Stock solution: (1.0 mL = 1.0 mg Li). Dissolve 5.324 g lithium carbonate, Li_2CO_3, in a minimum volume of 1:1 HCl and dilute to 1 liter with water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid as the samples used to prepare the samples and cover the range of expected concentrations in the samples.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Step 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation - The procedures for preparation of the sample are given in Chapter Three, Step 3.2.

7.2 See Method 7000, Step 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

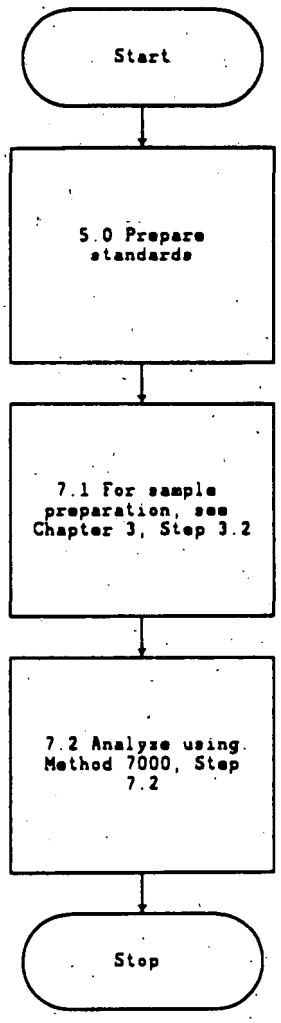
9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.1-2 mg/L at a wavelength of 670.8 nm.
Sensitivity: 0.04 mg/L.
Detection limit: 0.002 mg/L.

10.0 REFERENCES

1. Standard Methods for the Examination of Water and Wastewater, 16th ed.; Greenberg, A.E.; Trussell, R.R.; Clesceri, L.S., Eds.; American Water Works Association, Water Pollution Control Federation, American Public Health Association: Washington, DC, 1985.

METHOD 7430
LITHIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)



METHOD 7461

MANGANESE (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000.

3.2 Background correction must be used.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Drying time and temp: 30 sec at 125°C.

4.2.2 Ashing time and temp: 30 sec at 1000°C.

4.2.3 Atomizing time and temp: 10 sec at 2700°C.

4.2.4 Purge gas: Argon or nitrogen.

4.2.5 Wavelength: 279.5 nm.

4.2.6 Background correction: Required.

4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards

5.2.1 Stock solution - Dissolve 1.000 g manganese metal (analytical reagent grade) in 10 mL redistilled HNO_3 and dilute to 1 liter with water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibrations standards should be prepared using the same type of acid and at the same concentrations as in the sample after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Step 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample Preparation - The procedures for preparation of the sample are given in Chapter Three, Step 3.2.

7.2 See Method 7000, Step 7.3, Furnace Technique.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

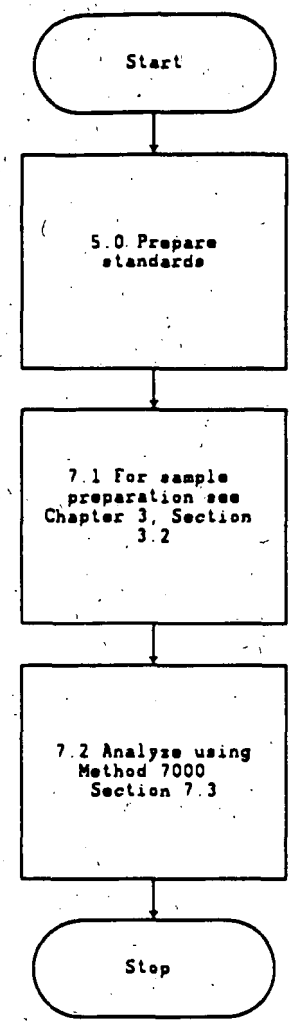
9.1 Precision and accuracy data are not available at this time.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 1-30 ug/L.
Detection limit: 0.2 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.


Start
5.0 Prepare standards
7.1 For sample preparation see Chapter 3, Section 3.2
7.2 Analyze using Method 7000 Section 7.3
Stop

METHOD 7470

MERCURY IN LIQUID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7470 is a cold-vapor atomic absorption procedure approved for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters. (Method 7470 can also be used for analyzing certain solid and sludge-type wastes; however, Method 7471 is usually the method of choice for these waste types.) All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the liquid samples must be prepared according to the procedure discussed in this method.

2.2 Method 7470, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from Type II water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 liter air/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 liter/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1.

4.9.1 The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system.

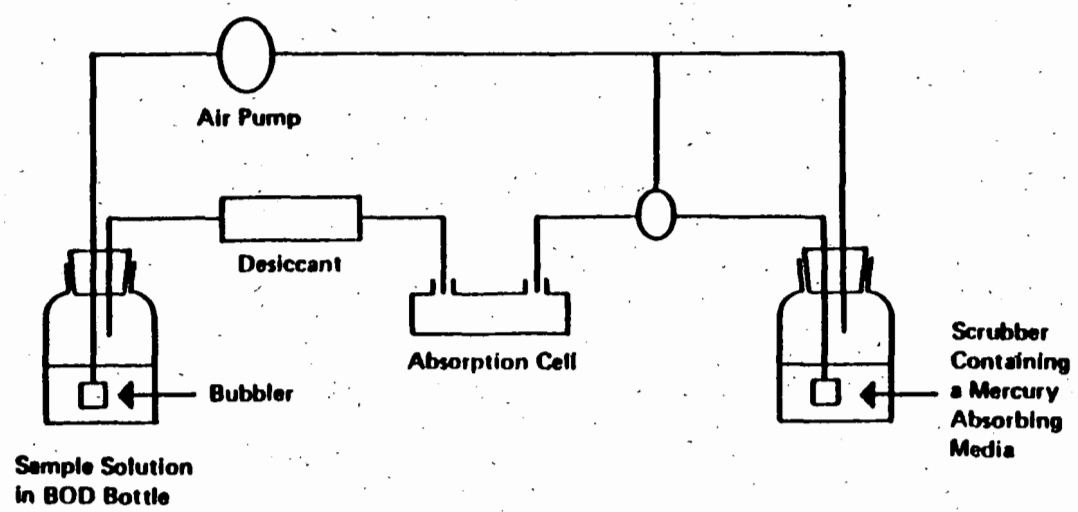


Figure 1. Apparatus for flameless mercury determination.

4.9.2 Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4; or
2. 0.25% Iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Sulfuric acid (H_2SO_4), concentrated: Reagent grade.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1.0 liter.

5.4 Nitric acid (HNO_3), concentrated: Reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

5.5 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N H_2SO_4. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

5.6 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in Type II water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

5.7 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of Type II water.

5.8 Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate in 100 mL of Type II water.

5.9 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of Type II water. Add 10 mL of concentrated HNO_3 and adjust the volume to 100.0 mL (1 mL = 1 mg Hg).

5.10 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 g per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before addition of the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH <2 with HNO_3. The suggested maximum holding times for these samples are 38 days in glass containers and 13 days in plastic containers.

6.4 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Transfer 100 mL, or an aliquot diluted to 100 mL, containing <1.0 g of mercury, to a 300-mL BOD bottle. Add 5 mL of H_2SO_4 and 2.5 mL of concentrated HNO_3, mixing after each addition. Add 15 mL of potassium permanganate solution to each sample bottle. Sewage samples may require additional permanganate. Ensure that equal amounts of permanganate are added to standards and blanks. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. After a delay of at least 30 sec, add 5 mL of stannous sulfate, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.2 Standard preparation: Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10.0-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles. Add enough Type II water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 to each bottle. Add 15 mL of $KMnO_4$ solution to each bottle and allow to stand at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized, wait 30 sec, add 5 mL of the stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.3 Analysis: At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter/min, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and

continue the aeration until the absorbance returns to its minimum valve. Close the bypass valve, remove the stopper and frit from the BOD bottle, and continue the aeration.

7.4 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

7.5 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions.

7.6 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.7 Calculate metal concentrations (1) by the method of standard additions, or (2) from a calibration curve. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.

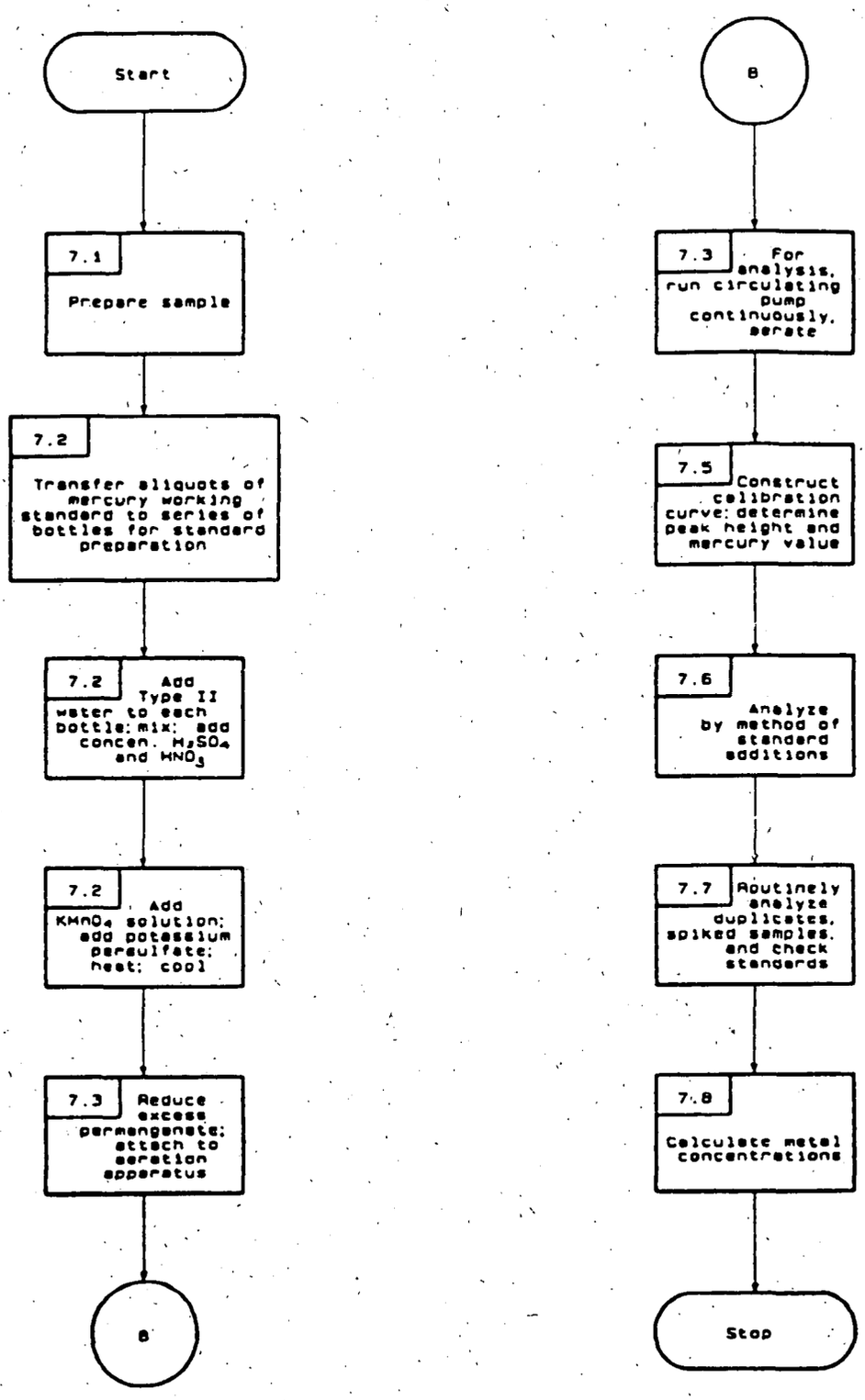
8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.1.



Revision 0
Date September 1986

METHOD 7470A

MERCURY IN LIQUID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7470 is a cold-vapor atomic absorption procedure approved for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters. (Method 7470 can also be used for analyzing certain solid and sludge-type wastes; however, Method 7471 is usually the method of choice for these waste types.) All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the liquid samples must be prepared according to the procedure discussed in this method.

2.2 Method 7470, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 liter air/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 liter/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1 of reference 1 or according to the instrument manufacturers instructions. The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system. Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4; or

2. 0.25% Iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

4.10 Hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.11 Graduated cylinder or equivalent.

5.0 REAGENTS

5.1 Reagent Water: Reagent water will be interference free. All references to water in this method will refer to reagent water unless otherwise specified.

5.2 Sulfuric acid (H_2SO_4), concentrated: Reagent grade.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1.0 liter.

5.4 Nitric acid (HNO_3), concentrated: Reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

5.5 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N H_2SO_4. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

5.6 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

5.7 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

5.8 Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate in 100 mL of reagent water.

5.9 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated HNO_3 and adjust the volume to 100.0 mL (1 mL = 1 mg Hg). Stock solutions may also be purchased.

5.10 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before addition of the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH <2 with HNO_3. The suggested maximum holding times for mercury is 28 days.

6.4 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Transfer 100 mL, or an aliquot diluted to 100 mL, containing <1.0 g of mercury, to a 300-mL BOD bottle or equivalent. Add 5 mL of H_2SO_4 and 2.5 mL of concentrated HNO_3, mixing after each addition. Add 15 mL of potassium permanganate solution to each sample bottle. Sewage samples may require additional permanganate. Ensure that equal amounts of permanganate are added to standards and blanks. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. After a delay of at least 30 sec, add 5 mL of stannous sulfate, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.2 Standard preparation: Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10.0-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles. Add enough reagent water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 to each bottle. Add 15 mL of $KMnO_4$ solution to each bottle and allow to stand at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized, wait 30 sec, add 5 mL of the stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.3 Analysis: At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter/min, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the stopper and frit from the BOD bottle, and continue the aeration. Because of instrument variation refer to the manufacturers recommended operating conditions when using this method.

7.4 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve. Duplicates, spiked samples, and check standards should be routinely analyzed.

7.5 Calculate metal concentrations (1) by the method of standard additions, or (2) from a calibration curve. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

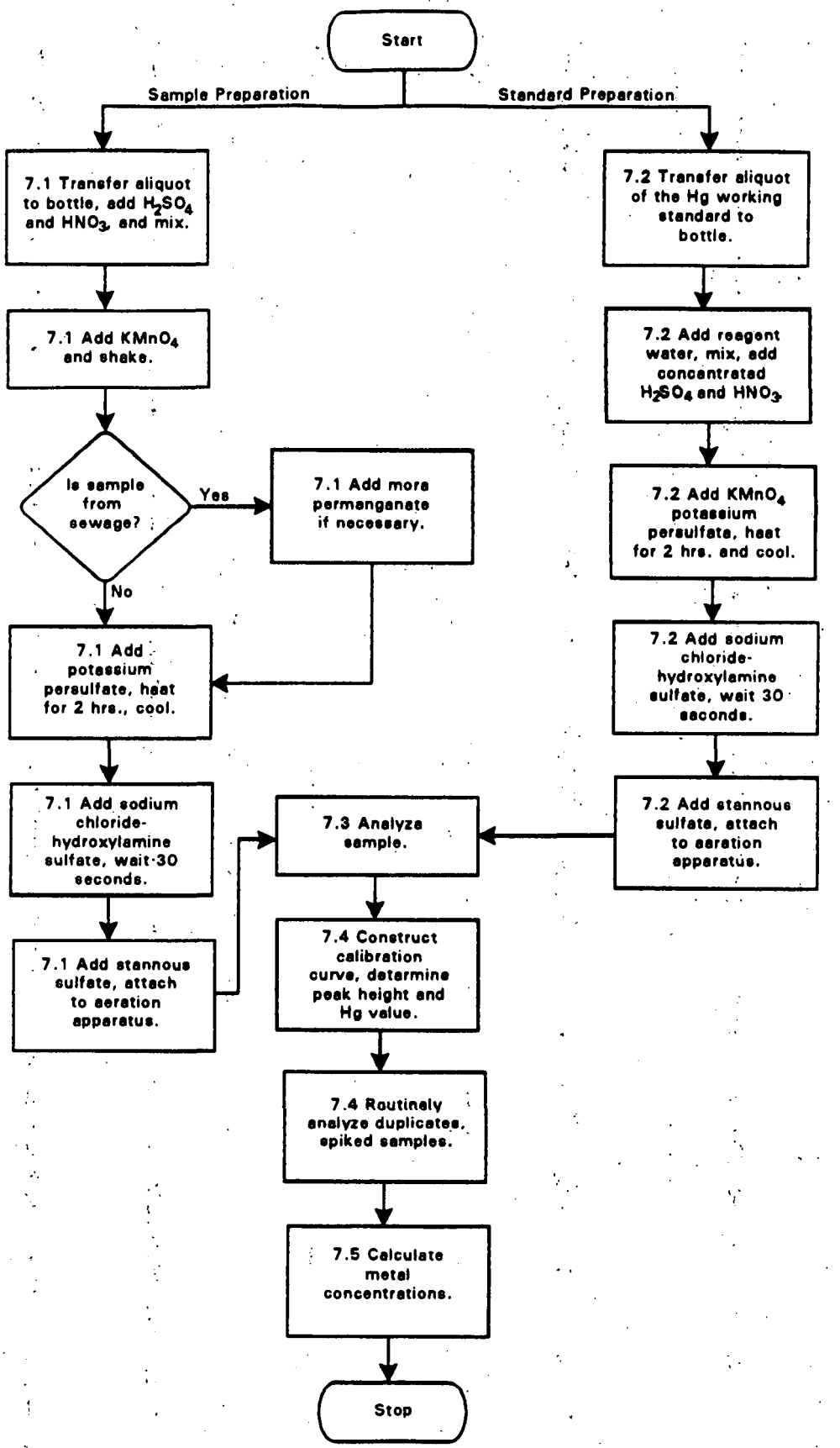
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.1.

METHOD 7470A
MERCURY IN LIQUID WASTE (MANUAL COLD-VAPOR TECHNIQUE)



METHOD 7471

MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

2.2 Method 7471, a cold-vapor atomic absorption method, is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from Type II water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 L/min air may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 L/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1.

4.9.1 The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system.

4.9.2 Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the

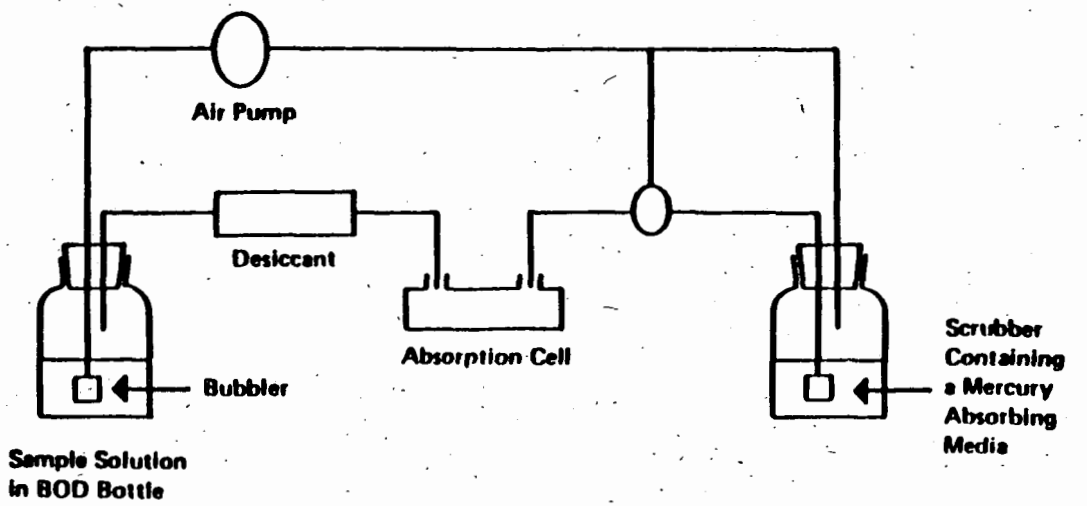


Figure 1. Apparatus for flameless mercury determination.

system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or
2. 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barneby and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1 liter.

5.4 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. A 10% solution of stannous chloride can be substituted for stannous sulfate.

5.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in Type II water and dilute to 100 mL. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

5.6 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of Type II water.

5.7 Mercury stock solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of Type II water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL (1.0 mL = 1.0 mg Hg).

5.8 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before adding the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH <2 with nitric acid.

6.4 For solids or semisolids, moisture may be driven off in a drying oven at a temperature of 60°C.

7.0 PROCEDURE

7.1 Sample preparation: Weigh triplicate 0.2-g portions of untreated sample and place in the bottom of a BOD bottle. Add 5 mL of Type II water and 5 mL of aqua regia. Heat 2 min in a water bath at 95°C. Cool; then add 50 mL Type II water and 15 mL potassium permanganate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

CAUTION: Do this addition under a hood, as Cl_2 could be evolved. Add 55 mL of Type II water. Treating each bottle individually, add 5 mL of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under step 7.4.

7.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 mL of concentrated H_2SO_4 and 2 mL of concentrated HNO_3 are added to the 0.2 g of sample. Add 5 mL of saturated $KMnO_4$ solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lb for 15 min. Cool, dilute to a volume of 100 mL with Type II water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under step 7.4.

7.3 Standard preparation: Transfer 0.0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles. Add enough Type II water to each bottle to make a total volume of 10 mL. Add 5 mL of aqua regia and heat 2 min in a water bath at 95°C. Allow the sample to cool; add 50 mL Type II water and 15 mL of $KMnO_4$ solution to each bottle and return to the water bath for 30 min. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 mL of Type II water. Treating each bottle individually, add 5 mL of stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Step 7.4.

7.4 Analysis: At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 L/min, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the fritted tubing from the BOD bottle, and continue the aeration.

7.5 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

7.6 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions (see Method 7000, Section 8.7).

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.

8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.5 of Methods for Chemical Analysis of Water and Wastes.

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

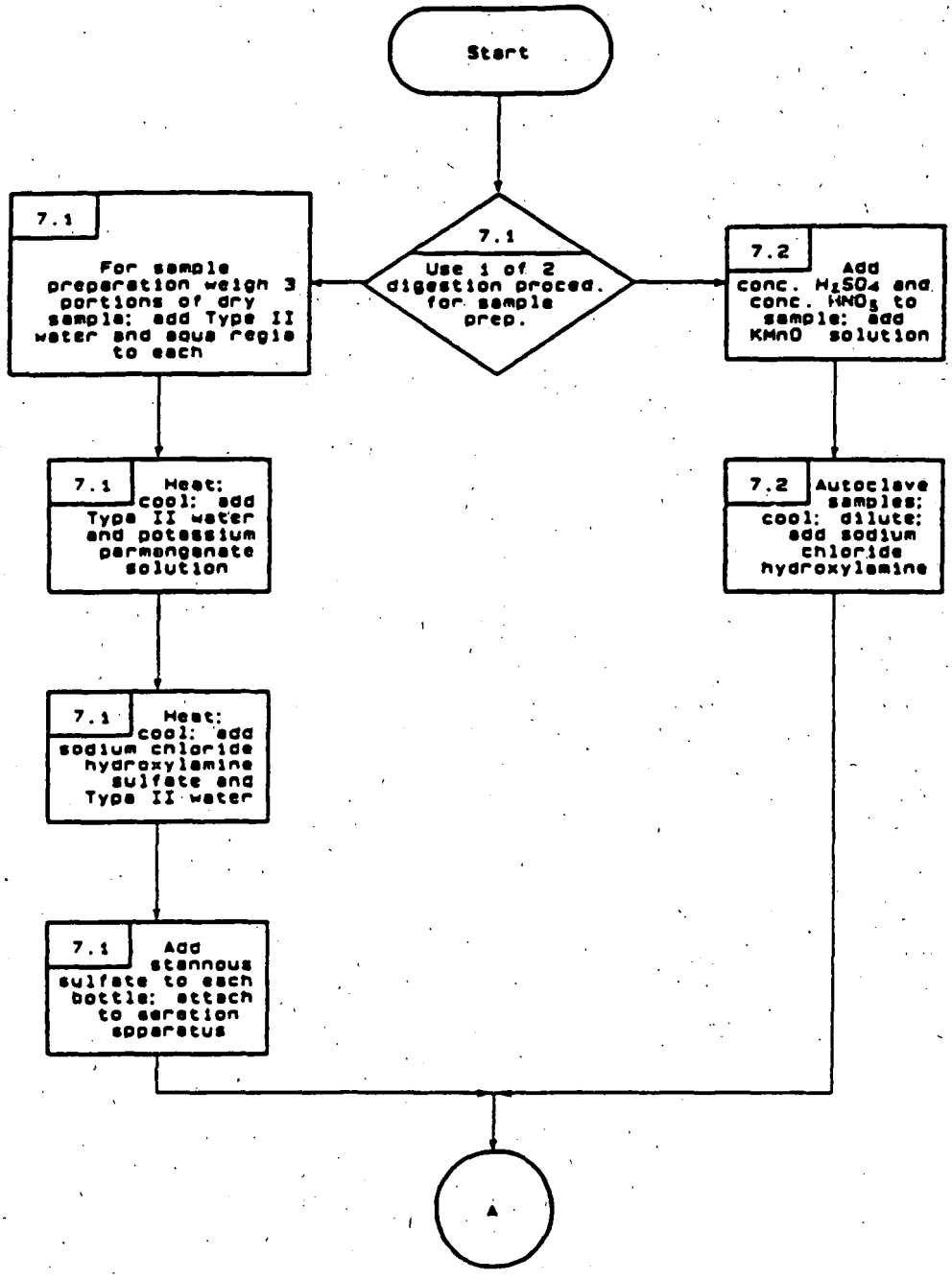
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.5.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	Not known	12, 12 ug/g
Wastewater treatment sludge	Not known	0.4, 0.28 ug/g

MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)



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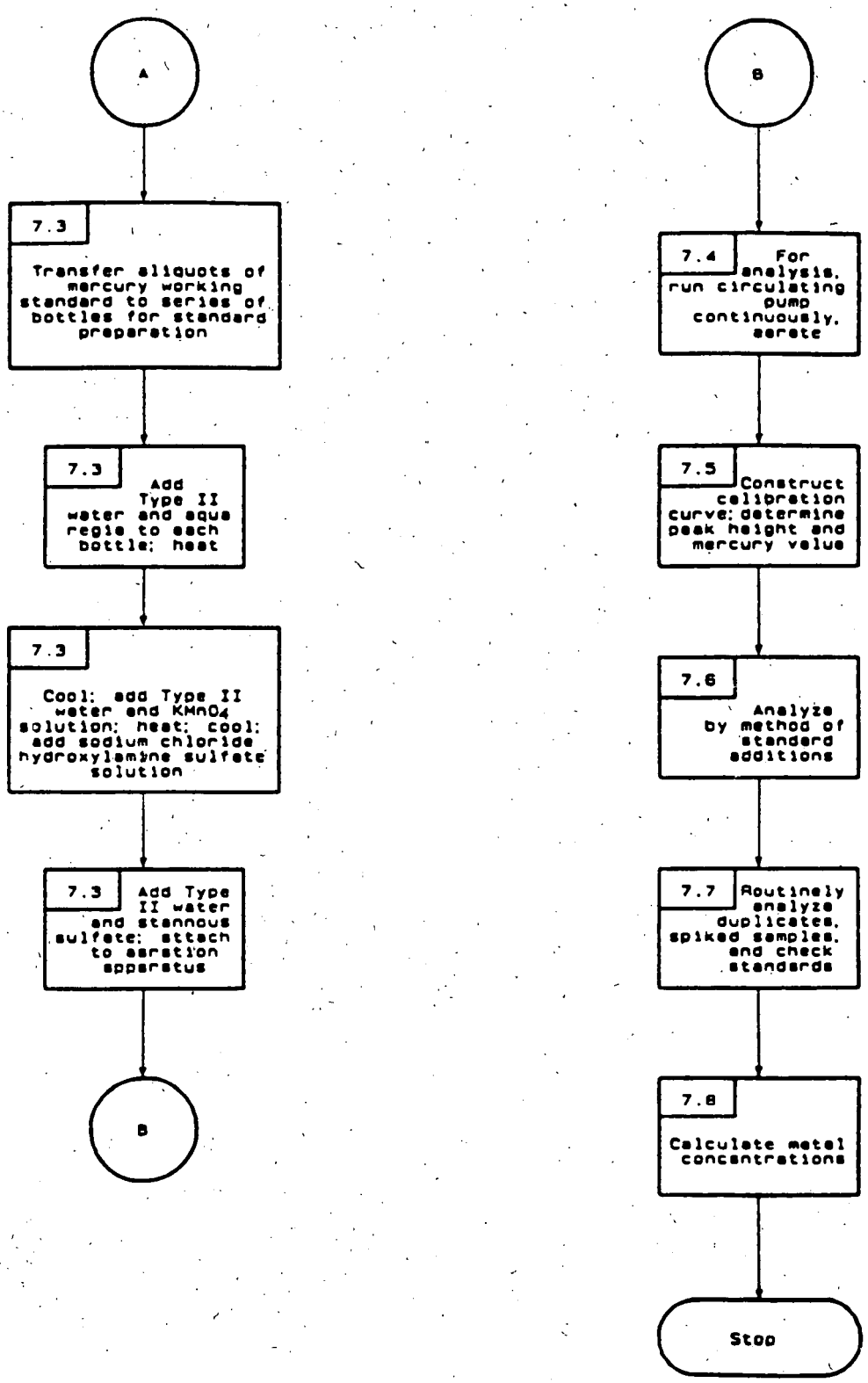
MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)
(Continued)



METHOD 7471A

MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

2.2 Method 7471, a cold-vapor atomic absorption method, is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical instrument detection limit (IDL) for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/Kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/Kg had no effect on recovery of mercury from spiked samples.

3.3 Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the

absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 L/min air may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 L/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1 of reference 1 or according to the instrument manufacturers instructions. The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system. Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or
2. 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barneby and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

4.10 Hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.11 Graduated cylinder or equivalent.

5.0 REAGENTS

5.1 Reagent Water: Reagent water will be interference free. All references to water in this method refer to reagent water unless otherwise specified.

5.2 Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1 liter.

5.4 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. A 10% solution of stannous chloride can be substituted for stannous sulfate.

5.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

5.6 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

5.7 Mercury stock solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL (1.0 mL = 1.0 mg Hg).

5.8 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before adding the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Non-aqueous samples shall be refrigerated, when possible, and analyzed as soon as possible."

7.0 PROCEDURE

7.1 Sample preparation: Weigh triplicate 0.2-g portions of untreated sample and place in the bottom of a BOD bottle. Add 5 mL of reagent water and 5 mL of aqua regia. Heat 2 min in a water bath at 95°C. Cool; then add 50 mL reagent water and 15 mL potassium permanganate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

> CAUTION: Do this addition under a hood, as Cl_2 could be evolved. Add 55 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under step 7.4.

7.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 mL of concentrated H_2SO_4 and 2 mL of concentrated HNO_3 are added to the 0.2 g of sample. Add 5 mL of saturated $KMnO_4$ solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lb for 15 min. Cool, dilute to a volume of 100 mL with reagent water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under step 7.4. Refer to the caution statement in section 7.1 for the proper protocol in reducing the excess permanganate solution and adding stannous sulfate.

7.3 Standard preparation: Transfer 0.0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles or equivalent. Add enough reagent water to each bottle to make a total volume of 10 mL. Add 5 mL of aqua regia and heat 2 min in a water bath at 95°C. Allow the sample to cool; add 50 mL reagent water and 15 mL of $KMnO_4$ solution to each bottle and return to the water bath for 30 min. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Step 7.4.

7.4 Analysis: At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 L/min, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the fritted tubing from the BOD bottle, and continue the aeration.

7.5 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve. Duplicates, spiked samples, and check standards should be routinely analyzed.

7.6 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into

account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.5 of Methods for Chemical Analysis of Water and Wastes.

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

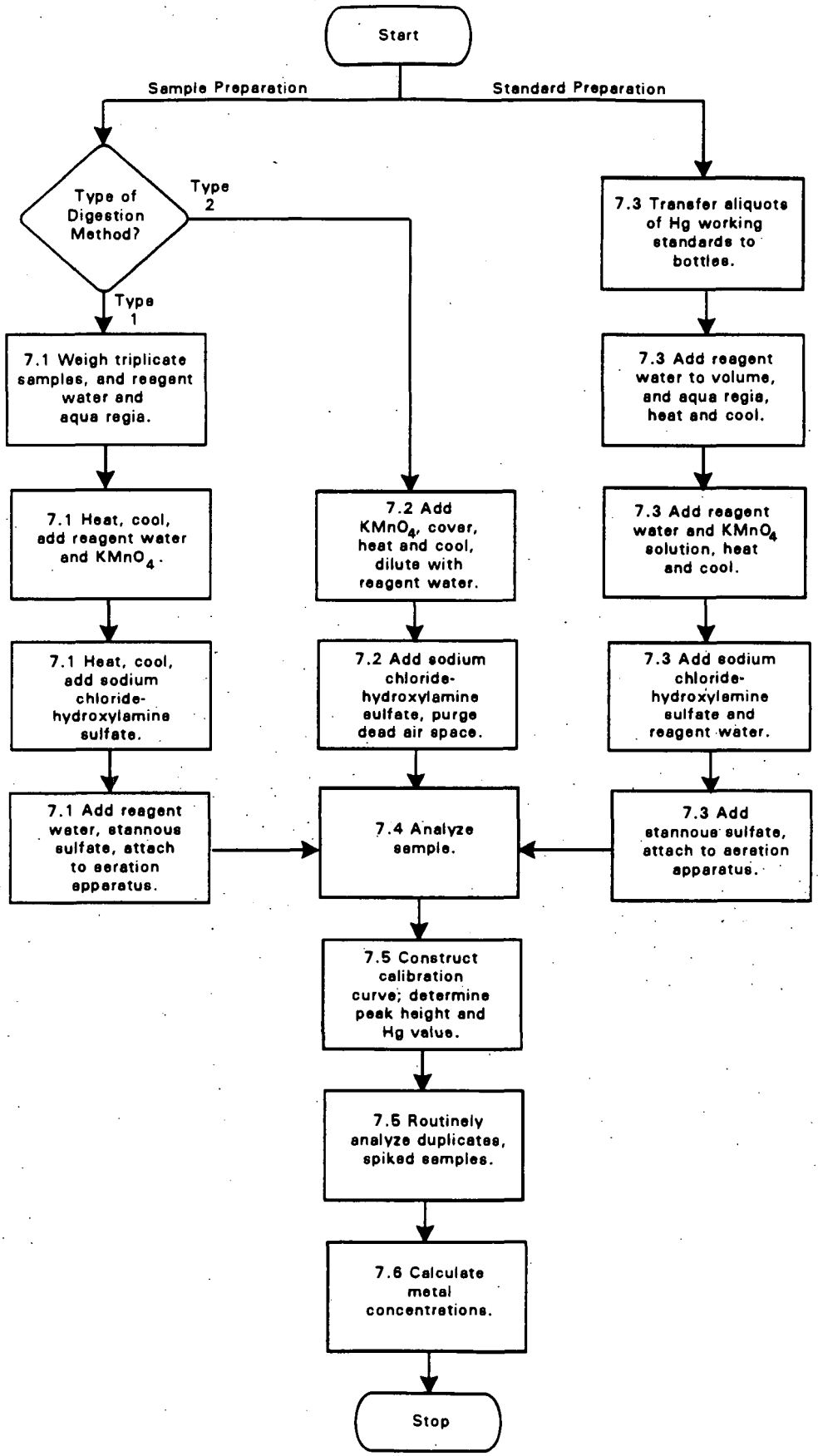
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.5.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	Not known	12, 12 ug/g
Wastewater treatment sludge	Not known	0.4, 0.28 ug/g

METHOD 7471A
MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)



METHOD 7741A

SELENIUM (ATOMIC ABSORPTION, GASEOUS HYDRIDE)

1.0 SCOPE AND APPLICATION

1.1 Method 7741 is an atomic absorption procedure that is approved for determining the concentration of selenium in wastes, mobility-procedure extracts, soils, and ground water, provided that the sample matrix does not contain high concentrations of chromium, copper, mercury, silver, cobalt, or molybdenum. All samples must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are employed to determine applicability of the method to a given waste. If interferences are present the analyst should consider using Method 7740.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric/sulfuric acid digestion procedure described in this method. Next, the selenium in the digestate is reduced to Se(IV) with tin chloride. The Se(IV) is then converted to a volatile hydride with hydrogen produced from a zinc/HCl or sodium borohydrate/HCl reaction.

2.2 The volatile hydride is swept into an argon-hydrogen flame located in the optical path of an atomic absorption spectrophotometer; the resulting absorbance is proportional to the selenium concentration.

2.3 The typical detection limit for this method is 0.002 mg/L.

3.0 INTERFERENCES

3.1 High concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver can cause analytical interferences.

3.2 Traces of nitric acid left following the sample work-up can result in analytical interferences. Nitric acid must be distilled off the sample by heating the sample until fumes of SO_3 are observed.

3.3 Elemental selenium and many of its compounds are volatile; therefore, certain samples may be subject to losses of selenium during sample preparation.

4.0 APPARATUS AND MATERIALS

4.1 100-mL beaker.

4.2 Electric hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.3 A commercially available zinc slurry hydride generator or a generator constructed from the following material (see Figure 1):

4.3.1 Medicine dropper: Fitted into a size "0" rubber stopper capable of delivering 1.5 mL.

4.3.2 Reaction flask: 50-mL, pear-shaped, with two 14/20 necks (Scientific Glass, JM-5835).

4.3.3 Gas inlet-outlet tube: Constructed from a micro cold-finger condenser (JM-3325) by cutting the portion below the 14/20 ground-glass joint.

4.3.4 Magnetic stirrer: To homogenize the zinc slurry.

4.3.5 Polyethylene drying tube: 10-cm, filled with glass wool to prevent particulate matter from entering the burner.

4.3.6 Flow meter: Capable of measuring 1 liter/min.

4.4 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190-800 nm, and provisions for interfacing with a strip-chart recorder and simultaneous background correction.

4.5 Burner: Recommended by the particular instrument manufacturer for the argon-hydrogen flame.

4.6 Selenium hollow cathode lamp or electrodeless discharge lamp.

4.7 Strip-chart recorder (optional).

5.0 REAGENTS

5.1 Reagent water: Water should be monitored for impurities. Reagent water will be interference free. All references to water will refer to reagent water.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.3 Concentrated sulfuric acid: Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.4 Concentrated hydrochloric acid: Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.5 Diluent: Add 100 mL 18 N H_2SO_4 and 400 mL concentrated HCl to 400 mL reagent water and dilute to a final volume of 1 liter with reagent water.

5.6 Potassium iodide solution: Dissolve 20 g KI in 100 mL reagent water.

5.7 Stannous chloride solution: Dissolve 100 g $SnCl_2$ in 100 mL of concentrated HCl.

5.8 Selenium standard stock solution: 1,000 mg/L solution may be purchased, or prepared as follows: Dissolve 0.3453 g of selenious acid (assay 94.6% of H_2SeO_3) in reagent water. Add to a 200-mL volumetric flask and bring to volume (1 mL = 1 mg Se).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile selenium compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation:

7.1.1 To a 50-mL aliquot of digested sample (or, in the case of extracts, a 50-mL sample) add 10 mL of concentrated HNO_3 and 12 mL of 18 N H_2SO_4. Evaporate the sample on a hot plate until white SO_3 fumes are observed (a volume of about 20 mL). Do not let it char. If it chars, stop the digestion, cool, and add additional HNO_3. Maintain an excess of HNO_3 (evidence of brown fumes) and do not let the solution darken because selenium may be reduced and lost. When the sample remains colorless or straw yellow during evolution of SO_3 fumes, the digestion is complete.

> Caution: Venting reaction vessels should be done with caution and only under a fume hood or well ventilated area.

7.1.2 Cool the sample, add about 25 mL reagent water, and again evaporate to SO_3 fumes just to expel oxides of nitrogen. Cool. Add 40 mL concentrated HCl and bring to a volume of 100 mL with reagent water.

7.2 Prepare working standards from the standard stock solutions. The following procedures provide standards in the optimum range.

7.2.1 To prepare a working stock solution, pipet 1 mL standard stock solution (see Paragraph 5.8) into a 1-liter volumetric flask. Bring to volume with reagent water containing 1.5 mL concentrated HNO_3/liter. The concentration of this solution is 1 mg Se/L (1 mL = 1 ug Se).

7.2.2 Prepare six working standards by transferring 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of the working stock solution (see Paragraph 7.2.1) into 100-mL volumetric flasks. Bring to volume with diluent. The concentrations of these working standards are 0, 5, 10, 15, 20, and 25 ug Se/L.

7.3 Standard additions:

7.3.1 Take the 15-, 20-, and 25-ug standards and transfer quantitatively 25 mL from each into separate 50-mL volumetric flasks. Add 10 mL of the prepared sample to each. Bring to volume with reagent water containing 1.5 mL HNO_3/liter.

7.3.2 Add 10 mL of prepared sample to a 50-mL volumetric flask. Bring to volume with reagent water containing 1.5 mL HNO_3/liter. This is the blank.

7.4 Follow the manufacturer's instructions for operating an argon-hydrogen flame. The argon-hydrogen flame is colorless; therefore, it may be useful to aspirate a low concentration of sodium to ensure that ignition has occurred.

7.5 The 196.0-nm wavelength shall be used for the analysis of selenium.

7.6 Transfer a 25-mL portion of the digested sample or standard to the reaction vessel. Add 0.5 mL $SnCl_2$ solution. Allow at least 10 min for the metal to be reduced to its lowest oxidation state. Attach the reaction vessel to the special gas inlet-outlet glassware. Fill the medicine dropper with 1.50 mL sodium borohydrate or zinc slurry that has been kept in suspension with the magnetic stirrer. Firmly insert the stopper containing the medicine dropper into the side neck of the reaction vessel. Squeeze the bulb to introduce the zinc slurry or sodium borohydrate into the sample or standard solution. The metal hydride will produce a peak almost immediately. When the recorder pen returns partway to the base line, remove the reaction vessel.

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

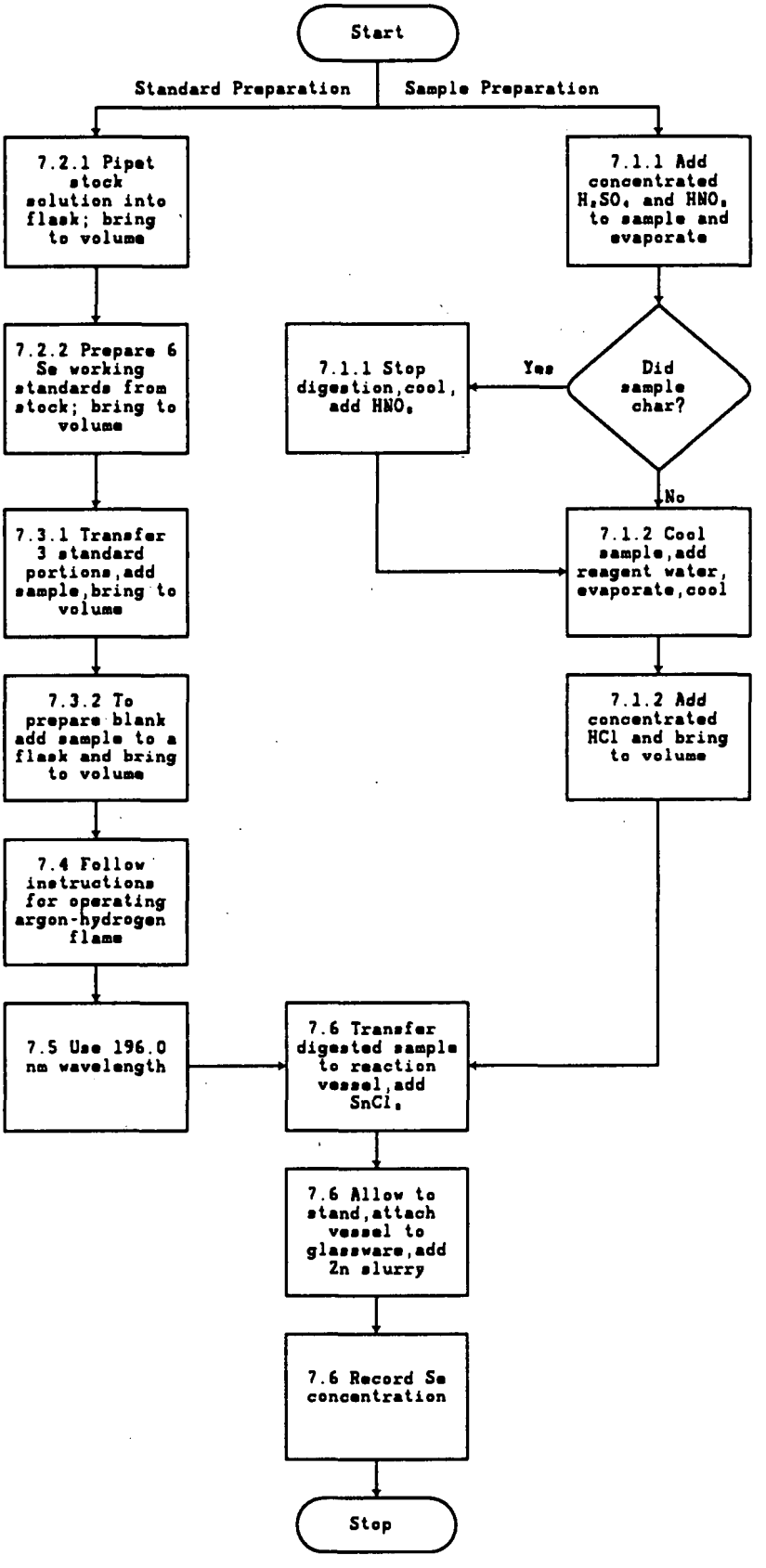
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 270.3 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 270.3.

METHOD 7741A
SELENIUM (ATOMIC ABSORPTION, GASEOUS HYDRIDE)



METHOD 7742

SELENIUM (ATOMIC ABSORPTION, BOROHYDRIDE REDUCTION)

1.0 SCOPE AND APPLICATION

1.1 Method 7742 is an atomic absorption procedure for determining 3 µg/L to 750 µg/L concentrations of selenium in wastes, mobility procedure extracts, soils, and ground water. Method 7742 is approved for sample matrices that contain a total of up to 1000 mg/L concentrations of cobalt, copper, iron, mercury, and nickel. A solid sample can contain up to 10% by weight of the interferents before exceeding 1000 mg/L in a digested sample. All samples including aqueous matrices must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are employed to determine the applicability of the method to a given waste.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric acid digestion procedure described in Method 3010 for aqueous and extract samples and the nitric/peroxide/hydrochloric acid digestion procedure described in Method 3050 (furnace AA option) for sediments, soils, and sludges. Excess peroxide is removed by evaporating samples to near-dryness at the end of the digestion followed by dilution to volume and degassing the samples upon addition of urea. The selenium is converted to the +4 oxidation state during digestion in HCl. After a 1:10 dilution, selenium is then converted to its volatile hydride using hydrogen produced from the reaction of the acidified sample with sodium borohydride in a continuous-flow hydride generator.

2.2 The volatile hydrides are swept into, and decompose in, a heated quartz absorption cell located in the optical path of an atomic absorption spectrophotometer. The resulting absorption of the lamp radiation is proportional to the selenium concentration.

2.3 The typical detection limit for this method is 3 µg/L.

3.0 INTERFERENCES

3.1 Very high (>1000 mg/L) concentrations of cobalt, copper, iron, mercury, and, nickel can cause analytical interferences through precipitation as reduced metals and associated blockage of transfer lines and fittings.

3.2 Traces of peroxides left following the sample work-up can result in analytical interferences. Peroxides must be removed by evaporating each sample to near-dryness followed by reacting each sample with urea and allowing sufficient time for degassing before analysis (see Sections 7.1 and 7.2).

3.3 Even after acid digestion, flame gases and organic compounds may remain in the sample. Flame gases and organic compounds can absorb at the analytical wavelengths and background correction should be used.

4.0 APPARATUS AND MATERIALS

4.1 Electric hot plate: Large enough to hold at least several 100 mL Pyrex digestion beakers.

4.2 A continuous-flow hydride generator: A commercially available continuous-flow sodium borohydride/HCl hydride generator or a generator constructed similarly to that shown in Figure 1 (P. S. Analytical or equivalent).

4.2.1 Peristaltic Pump: A four-channel, variable-speed peristaltic pump to permit regulation of liquid-stream flow rates (Ismatec Reglo-100 or equivalent). Pump speed and tubing diameters should be adjusted to provide the following flow rates: sample/blank flow = 4.2 mL/min; borohydride flow = 2.1 mL/min.

4.2.2 Sampling Valve (optional): A sampling valve (found in the P. S. Analytical Hydride Generation System or equivalent) that allows switching between samples and blanks (rinse solution) without introduction of air into the system will provide more signal stability.

4.2.3 Transfer Tubing and Connectors: Transfer tubing (1 mm I.D.), mixing T's, and connectors are made of fluorocarbon (PFA or TFM) and are of compatible sizes to form tight, leak-proof connections (Latchat, Technicon, etc. flow injection apparatus accessories or equivalent).

4.2.4 Mixing Coil: A 20-turn coil made by wrapping transfer tubing around a 1-cm diameter by 5-cm long plastic or glass rod (see Figure 1).

4.2.5 Mixing Coil Heater, if appropriate: A 250-mL Erlenmeyer flask containing 100 mL of water heated to boiling on a dedicated one-beaker hotplate (Corning PC-35 or equivalent). The mixing coil in 4.2.4 is immersed in the boiling water to speed kinetics of the hydride forming reactions and increase solubility of interfering reduced metal precipitates.

4.2.6 Gas-Liquid Separator: A glass apparatus for collecting and separating liquid and gaseous products (P. S. Analytical accessory or equivalent) which allows the liquid fraction to drain to waste and gaseous products above the liquid to be swept by a regulated carrier gas (argon) out of the cell for analysis. To avoid undue carrier gas dilution, the gas volume above the liquid should not exceed 20 mL. See Figure 1 for an acceptable separator shape.

4.2.7 Condensor: Moisture picked up by the carrier gas must be removed before encountering the hot absorbance cell. The moist carrier gas with the hydrides is dried by passing the gasses through a small (< 25 mL) volume condensor coil (Ace Glass Model 6020-02 or equivalent) that is cooled to 5°C by a water chiller (Neslab RTE-110 or equivalent). Cool tap-water in place of a chiller is acceptable.

4.2.8 Flow Meter/Regulator: A meter capable of regulating up to 1 L/min of argon carrier gas is recommended.

4.3 Absorbance Cell: A 17-cm or longer quartz tube T-cell (windowless is strongly suggested) is recommended, as shown in Figure 1 (Varian Model VGA-76 accessory or equivalent). The cell is held in place by a holder that positions the cell about 1 cm over a conventional AA air-acetylene burner head. In operation, the cell is heated to around 900°C.

4.4 Atomic absorption spectrophotometer: Single- or dual- channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with an appropriate recording device.

4.5 Burner: As recommended by the particular instrument manufacturer for an air-acetylene flame. An appropriate mounting bracket attached to the burner that suspends the quartz absorbance cell between 1 and 2 cm above the burner slot is required.

4.6 Selenium hollow cathode lamp or selenium electrodeless discharge lamp and power supply. Super-charged hollow-cathode lamps or EDL lamps are recommended for maximum sensitivity.

4.7 Strip-chart recorder (optional): Connect to output of spectrophotometer.

5.0 REAGENTS

5.1 Reagent water : Water must be monitored for impurities. Refer to Chapter 1 for definition of Reagent water.

5.2 Concentrated nitric acid (HNO_3): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.3 30% Hydrogen peroxide (H_2O_2): Peroxide must be a tin-free grade.

5.4 Concentrated hydrochloric acid (HCl): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.5 Diluent solution: A 3% HCl solution in reagent water must be prepared as a diluent solution if excessive levels of analytes or interfering metals are found in the undiluted samples.

5.6 Urea (H_2NCONH_2): A 5.00-g portion of reagent grade urea must be added to a 25-mL aliquot of each sample for removal of excess peroxide through degassing (see Section 7.2).

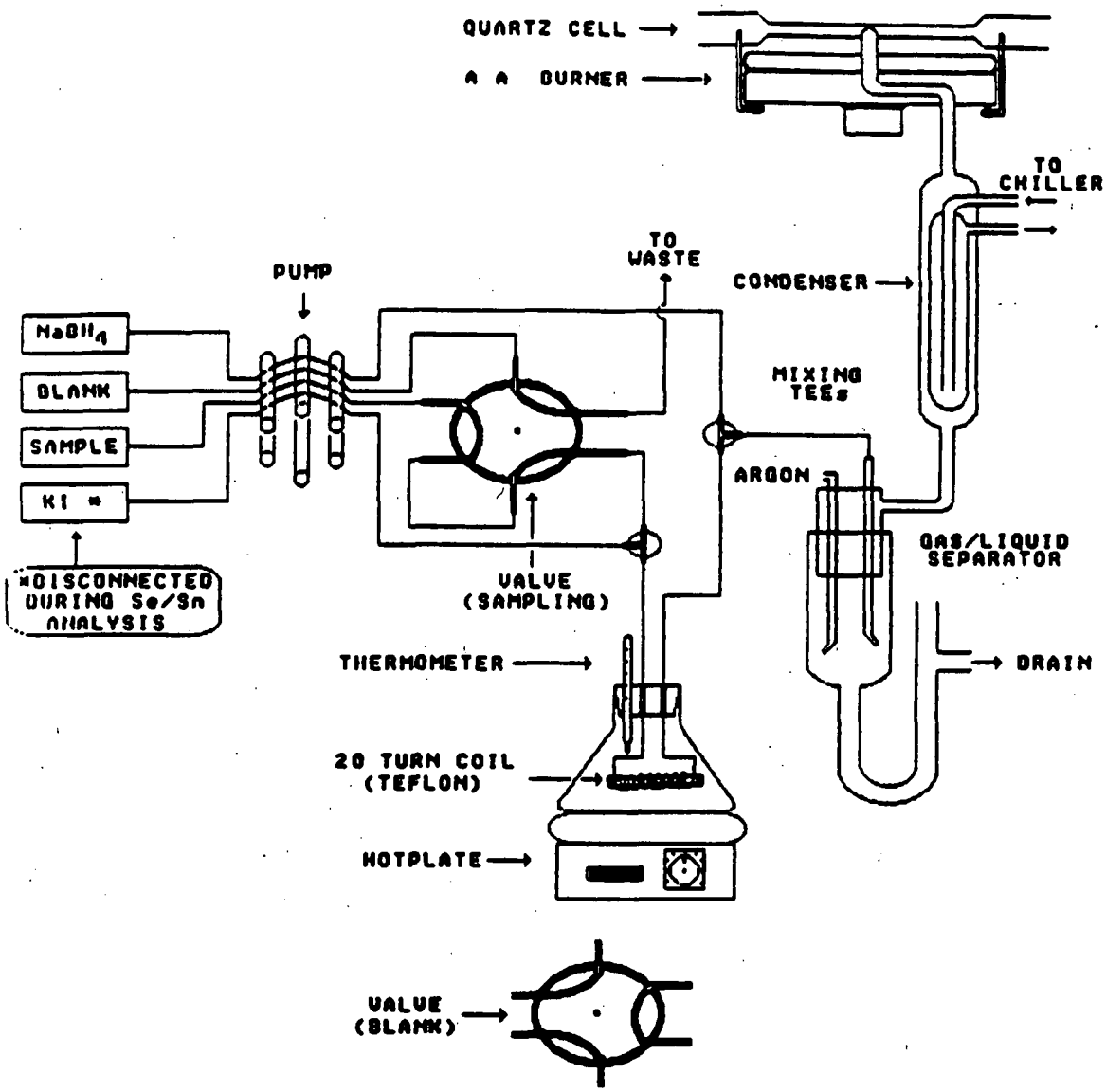


Figure 1. Continuous-flow sodium borohydride/hydride generator apparatus setup and an AAS sample introduction system

5.7 4% Sodium Borohydride ($NaBH_4$): A 4 % sodium borohydride solution (20 g reagent-grade $NaBH_4$ plus 2 g sodium hydroxide dissolved in 500 mL of reagent water) must be prepared for conversion of the selenium to its hydride.

5.8 Selenium solutions:

5.8.1 **Selenium standard stock solution** (1,000 mg/L): Either procure certified aqueous standards from a supplier and verify by comparison with a second standard, or dissolve 0.3453 g of selenious acid (assay 96.6% of H_2SeO_3) in 200 mL of reagent water (1 mL = 1 mg Se).

5.8.2 **Selenium working stock solution:** Pipet 1 mL selenium standard stock solution into a 1 L volumetric flask and bring to volume with reagent water containing 1.5 mL concentrated HNO_3/liter. The concentration of this solution is 1 mg Se/L (1 mL = 1 μg Se).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile selenium compounds are suspected to be present in the samples.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Place a 100-mL portion of an aqueous sample or extract or 1.000 g of a dried solid sample in a 250-mL digestion beaker. Digest aqueous samples and extracts according to Method 3010. Digest solid samples according to Method 3050 (furnace AA option) with the following modifications: add 5 mL of concentrated hydrochloric acid just prior to the final volume reduction stage to aid in conversion of selenium to its plus four state; the final volume reduction should be to less than 5 mL but not to dryness to adequately remove excess hydrogen peroxide (see note). After dilution to volume, further dilution with diluent may be necessary if the analyte is known to exceed 750 μg/L or if interferents are expected to exceed a total of 1000 mg/L in the digestate.

> Note: For solid digestions, the volume reduction stage is critical to obtain accurate data. Close monitoring of each sample is necessary when this critical stage in the digestion is reached.

7.2 Prepare samples for hydride analysis by adding 1.00 g urea, and 20 mL concentrated HCl to a 5.00 mL aliquot of digested sample in a 50-mL volumetric flask. Heat in a water bath to dissolve salts and reduce selenium (at least 30 minutes is suggested). Bring flask to volume with reagent water before analyzing. A ten-fold dilution correction must be made in the final concentration calculations.

7.3 Prepare working standards from the standard stock selenium solution. Transfer 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of standard to 100-mL volumetric flasks and bring to volume with diluent. These concentrations will be 0, 5, 10, 15, 20, and 25 μg Se/L.

7.4 If EP extracts (Method 1310) are being analyzed for selenium, the method of standard additions must be used. Spike appropriate amounts of working standard selenium solution to three 25 mL aliquots of each unknown. Spiking volumes should be kept less than 0.250 mL to avoid excessive spiking dilution errors.

7.5 Set up instrumentation and hydride generation apparatus and fill reagent containers. The sample and blank flows should be set around 4.2 mL/min, and the borohydride flow around 2.1 mL/min. The argon carrier gas flow is adjusted to about 200 mL/min. For the AA, use the 196.0-nm wavelength and 2.0-nm slit width (or manufacturer's recommended slit-width) with background correction. Begin all flows and allow the instrument to warm-up according to the instrument manufacturer's instructions.

7.6 Place sample feed line into a prepared sample solution and start pump to begin hydride generation. Wait for a maximum steady-state signal on the strip-chart recorder. Switch to blank sample and watch for signal to decline to baseline before switching to the next sample and beginning the next analysis. Run standards first (low to high), then unknowns. Include appropriate QA/QC solutions, as required. Prepare calibration curves and convert absorbances to concentration. See following analytical flowchart.

CAUTION: The hydride of selenium is very toxic. Precautions must be taken to avoid inhaling the gas.

7.7 If the method of standard additions was employed, plot the measured concentration of the spiked samples and unspiked sample versus the spiked concentrations. The spiked concentration axis intercept will be the method of standard additions concentration. If the plot does not result in a straight line, a nonlinear interference is present. This problem can sometimes be overcome by dilution or addition of other reagents if there is some knowledge about the waste. If the method of standard additions was not required, then the concentration is determined from a standard calibration curve.

8.0 QUALITY CONTROL

8.1 Refer to Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

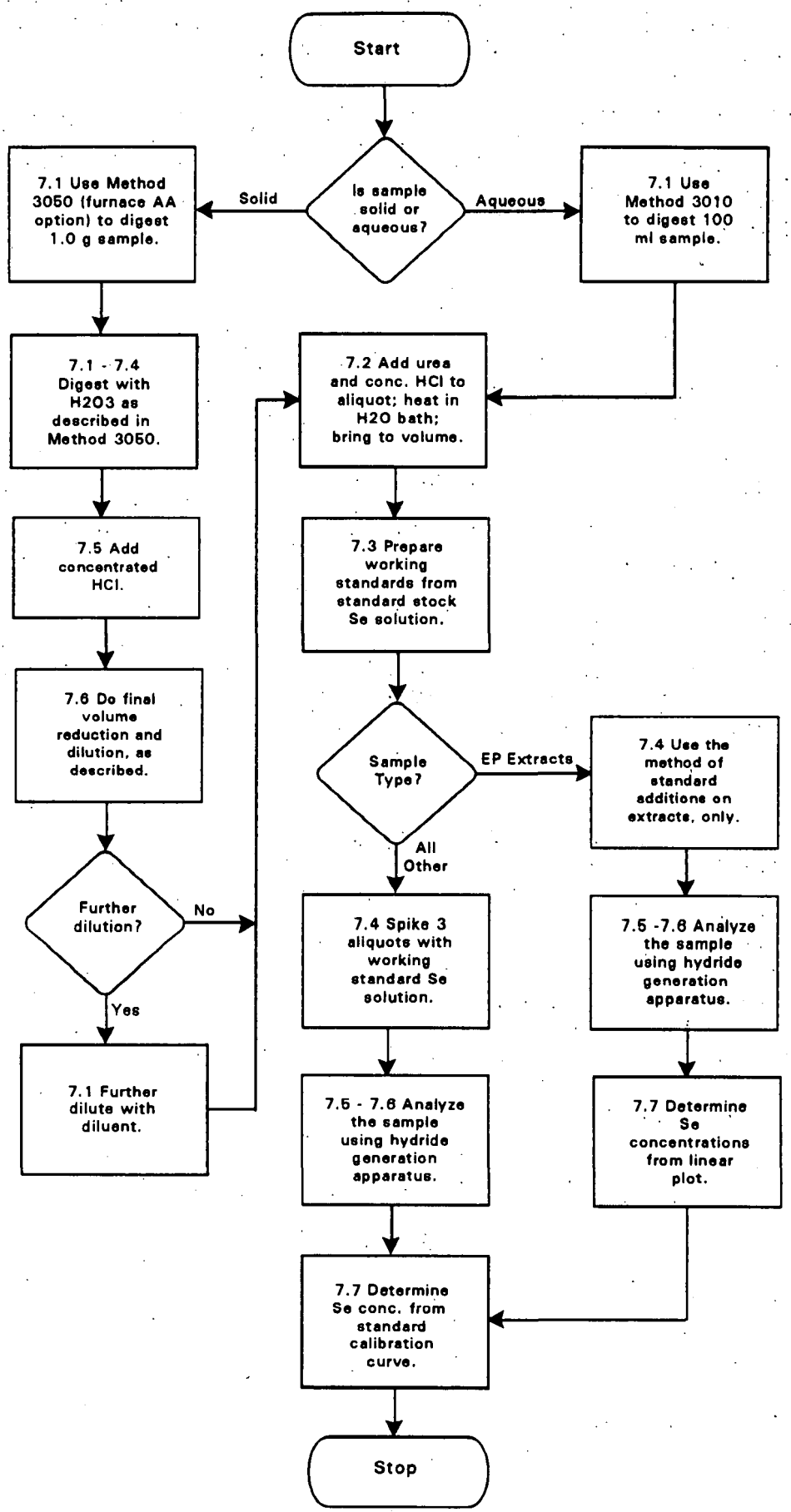
9.1 The relative standard deviation obtained by a single laboratory for 7 replicates of a contaminated soil was 18% for selenium at 8.2 ug/L in solution. The average percent recovery of the analysis of an 2 μg/L spike on ten different samples is 100.5% for selenium.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.3.

2. "Evaluation of Hydride Atomic Absorption Methods for Antimony, Arsenic, Selenium, and Tin", an EMSL-LV internal report under Contract 68-03-3249, Job Order 70.16, prepared for T. A. Hinners by D. E. Dobb, and J. D. Lindner of Lockheed Engineering and Sciences Co., and L. V. Beach of the Varian Corporation.

METHOD 7742
SELENIUM (ATOMIC ABSORPTION, BOROHYDRIDE REDUCTION)



7760A

METHOD 7760A

SILVER (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 Method 7760 is an atomic absorption procedure approved for determining the concentration of silver (CAS Registry Number 7440-22-4) in wastes, mobility procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7760, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to the acid-digestion procedure described in this method.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an air/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the silver concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.01 mg/L; typical sensitivity is 0.06 mg/L.

3.0 INTERFERENCES

3.1 Background correction is required because nonspecific absorption and light scattering may occur at the analytical wavelength.

3.2 Silver nitrate solutions are light-sensitive and have the tendency to plate out on container walls. Thus silver standards should be stored in brown bottles.

3.3 Silver chloride is insoluble; therefore, hydrochloric acid should be avoided unless the silver is already in solution as a chloride complex.

3.4 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer: Single- or dual-channel, single- or double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Silver hollow cathode lamp.

4.3 Strip-chart recorder (optional).

4.4 Graduated cylinder or equivalent.

4.5 Hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95°C.

4.6 Ribbed watchglasses or equivalent.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water is interference free. All references to water in the method refer to reagent water unless otherwise specified.

5.3 Nitric Acid (concentrated), HNO_3.

5.4 Ammonium Hydroxide (concentrated), NH_4OH.

5.5 Silver Stock Standard Solution (1,000 mg/L), $AgNO_3$. Dissolve 0.7874 g anhydrous silver nitrate in water. Add 5 mL HNO_3 and bring to volume in a 500-mL volumetric flask (1 mL = 1 mg Ag). Alternatively, procure a certified aqueous standard from a supplier and verify by comparison with a second standard.

5.6 Silver working standards - These standards should be prepared from silver stock solution to be used as calibration standards at the time of analysis. These standards should be prepared with nitric acid and at the same concentrations as the analytical solution.

5.7 Iodine solution (1N). Dissolve 20 g potassium iodide (KI), in 50 mL of water. Add 12.7 g iodine (I_2) and dilute to 100 mL. Store in a brown bottle.

5.8 Cyanogen iodide solution. Add 4.0 mL ammonium hydroxide, 6.5 g potassium cyanide (KCN), and 5.0 mL of iodine solution to 50 mL of water. Mix and dilute to 100 mL with water. Do not keep longer than 2 weeks.

<u>CAUTION</u>: This reagent cannot be mixed with any acid solutions because toxic hydrogen cyanide will be produced.

5.9 Air.

5.10 Acetylene.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH < 2 with nitric acid.

6.4 When possible, standards and samples should be stored in the dark and in brown bottles.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation - Aqueous samples should be prepared according to Steps 7.2 and 7.3. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 Preparation of aqueous samples

7.2.1 Transfer a representative aliquot of the well-mixed sample to a beaker and add 3 mL of concentrated HNO_3. Cover the beaker with a ribbed watch glass. Place the beaker on a hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil. DO NOT BAKE. Cool the beaker and add another 3-mL portion of concentrated HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

<u>NOTE</u>: If the sample contains thiosulfates, this step may result in splatter of sample out of the beaker as the sample approaches dryness. This has been reported to occur with certain photographic types of samples.

7.2.2 Continue heating, adding additional acid, as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add a small quantity of HNO_3 so that the final dilution contains 0.5% (v/v) HNO_3 and warm the beaker to dissolve any precipitate or residue resulting from evaporation.

7.2.3 Wash down the beaker walls and watch glass with water and, when necessary, filter the sample to remove silicates and other insoluble material that could clog the nebulizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis.

7.3 If plating out of AgCl is suspected, the precipitate can be redissolved by adding cyanogen iodide to the sample. This can be done only after digestion and after neutralization of the sample to a pH > 7 to prevent formation of toxic cyanide under acid conditions. In this case do not adjust the sample volume to the predetermined value until the sample has been neutralized to pH > 7 and cyanogen iodide has been added. If cyanogen iodide addition to the sample is necessary, then the standards must be treated in the same manner. Cyanogen iodide must not be added to the acidified silver standards. New standards must be made, as directed in Steps 5.5 and 5.6, except that the acid addition step must be omitted. For example, to obtain a 100 mg/L working standard, transfer 10 mL of stock solution to a small beaker. Add water to make about 70 mL. Make the solution basic (pH above 7) with ammonium hydroxide. Rinse the pH meter electrodes into the solution with water. Add 1 mL cyanogen iodide and allow to stand 1 hour. Transfer quantitatively to a 100-mL volumetric flask and bring to volume with water.

CAUTION: CNI reagent can be added only after digestion to prevent formation of toxic cyanide under acidic conditions. CNI reagent must not be added to the acidified silver standards.

NOTE: Once the sample or sample aliquot has been treated with the CNI reagent and diluted per instruction, the solution has a cyanide concentration of approximately 260 mg/L. A solution of that cyanide concentration must be considered a potential hazardous waste and must be disposed of using an approved safety plan in accordance with local authority requirements. Until such time that a detailed disposal plan can be fully documented and approved, the use of the CNI reagent should be avoided.

7.4 The 328.1 nm wavelength line and background correction shall be employed.

7.5 An oxidizing air-acetylene flame shall be used.

7.6 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 272.1 of "Methods for Chemical Analysis of Water and Wastes."

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.

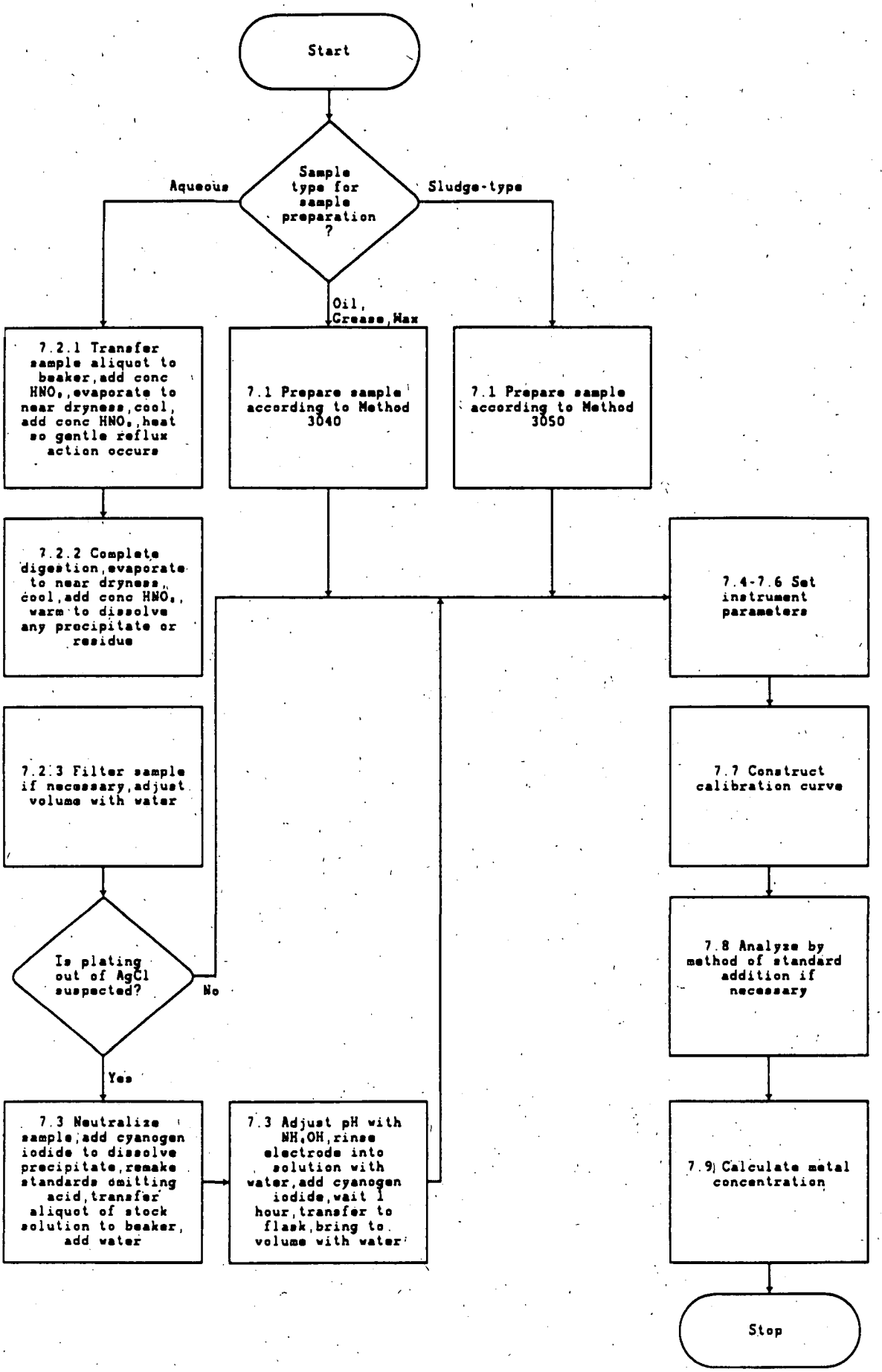
2. Gaskill, A., Compliation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, December 1987.

3. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

4. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ATSM: Philadelphia, PA, 1985; D1193-77.

TABLE 1.
METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	3050	2.3, 1.6 mg/Kg
Emission control dust	3050	1.8, 4.2 mg/Kg


Start
Sample type for sample preparation ?
Aqueous
Oil, Grease, Wax
Sludge-type
7.2.1 Transfer sample aliquot to beaker, add conc HNO3, evaporate to near dryness, cool, add conc HNO3, heat so gentle reflux action occurs
7.1 Prepare sample according to Method 3040
7.1 Prepare sample according to Method 3050
7.2.2 Complete digestion, evaporate to near dryness, cool, add conc HNO3, warm to dissolve any precipitate or residue
7.4-7.6 Set instrument parameters
7.2.3 Filter sample if necessary, adjust volume with water
7.7 Construct calibration curve
Is plating out of AgCl suspected?
No
Yes
7.8 Analyze by method of standard addition if necessary
7.3 Neutralize sample, add cyanogen iodide to dissolve precipitate, remake standards omitting acid, transfer aliquot of stock solution to beaker, add water
7.3 Adjust pH with NH4OH, rinse electrode into solution with water, add cyanogen iodide, wait 1 hour, transfer to flask, bring to volume with water
7.9 Calculate metal concentration
Stop

METHOD 7761

SILVER (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7761 is an atomic absorption procedure approved for determining the concentration of silver in wastes, mobility procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution procedure.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, silver analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction must be employed to avoid erroneously high results.

3.3 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at higher atomization temperatures.

3.4 Silver nitrate solutions are light sensitive and have the tendency to plate out on container walls. Thus, silver standards should be stored in brown bottles.

3.5 Silver chloride is insoluble; therefore, hydrochloric acid should be avoided unless the silver is already in solution as a chloride complex.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument Parameters (General):

4.2.1 Drying Time and Temp: 30 sec at 125°C.

4.2.2 Ashing Time and Temp: 30 sec at 400°C.

4.2.3 Atomizing Time and Temp: 10 sec at 2700°C.

4.2.4 Purge Gas Atmosphere: Argon.

4.2.5 Wavelength: 328.1 nm.

4.2.6 Background Correction: Required.

4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Silver Stock Standard Solution (1,000 mg/L), $AgNO_3$. Dissolve 0.7874 g anhydrous silver nitrate ($AgNO_3$), analytical reagent grade, water. Add 5 mL concentrated nitric acid (HNO_3) and bring to volume in a 500 mL volumetric flask (1 mL = 1 mg Ag). Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.3 Silver working standards - These standards should be prepared with nitric acid such that the final acid concentration is 0.5% (v/v) HNO_3.

5.4 Ammonium hydroxide (concentrated), (NH_4OH). Base should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.5 Iodine solution (1N). Dissolve 20 g potassium iodide (KI), analytical reagent grade, in 50 mL water. Add 12.7 g iodine (I_2), analytical reagent grade, and dilute to 100 mL with water. Store in a brown bottle.

5.6 Cyanogen iodide solution. To 50 mL water add 4.0 mL concentrated NH_4OH, 6.5 g potassium cyanide (KCN), and 5.0 mL of iodine solution. Mix and dilute to 100 mL with water. Do not keep longer than 2 weeks.

CAUTION: This reagent cannot be mixed with any acid solutions since highly toxic hydrogen cyanide will be produced.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Step 3.1.3, Sample Handling and Preservation.

6.2 Standards and samples should be stored in the dark, in brown bottles, and refrigerated.

7.0 PROCEDURE

7.1 Sample preparation - Aqueous samples should be prepared according to Steps 7.2 and 7.3. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 Preparation of aqueous samples

7.2.1 Transfer a representative aliquot of the well-mixed sample to a beaker and add 3 mL of concentrated HNO_3. Cover the beaker with a watch glass. Place the beaker on the hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil. DO NOT BAKE. Cool the beaker and add another 3-mL portion of concentrated HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

NOTE: If the sample contains thiosulfates, this step may result in splatter of sample out of the beaker as the sample approaches dryness. This has been reported to occur with certain types of photographic wastes.

7.2.2 Continue heating, adding additional acid, as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add a small quantity of HNO_3 so that the final dilution contains 0.5% (v/v) HNO_3 and warm the beaker to dissolve any precipitate or residue resulting from evaporation.

7.2.3 Wash down the beaker walls and watch glass with water and, when necessary, filter the sample to remove silicates and other insoluble material that could clog the nebulizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis.

7.3 If plating out of AgCl is suspected, the precipitate can be redissolved by adding cyanogen iodide to the sample. This can be done only after digestion and after neutralization of the sample to a pH > 7 to prevent formation of toxic cyanide under acid conditions. In this case, do not adjust the sample volume to the predetermined value until the sample has been neutralized to pH > 7 and cyanogen iodide has been added. If cyanogen iodide addition to the sample is necessary, then the standards must be treated in the same manner. Cyanogen iodide must not be added to the acidified silver standards. New standards must be made, as directed in Step 5.2, except that the acid addition step must be omitted. For example, to obtain a 100 mg/L working standard, transfer 10 mL of stock solution to a small beaker. Add water to make about 70 mL. Make the solution basic (pH above 7) with NH_4OH. Rinse the pH meter electrodes into the

solution with water. Add 1 mL cyanogen iodide and allow to stand 1 hour. Transfer quantitatively to a 100-mL volumetric flask and bring to volume with water.

CAUTION: CNI reagent can be added only after digestion to prevent formation of toxic cyanide under acidic conditions. CNI reagent must not be added to the acidified silver standards.

NOTE: Once the sample or sample aliquot has been treated with the CNI reagent and diluted per instruction, the solution has a cyanide concentration of approximately 260 mg/L. A solution of that cyanide concentration must be considered a potential hazardous waste and must be disposed of using an approved safety plan in accordance with local authority requirements. Until such time that a detailed disposal plan can be fully documented and approved, the use of the CNI reagent should be avoided.

7.4 The 328.1-nm wavelength line and background correction shall be used.

7.5 Following the manufacturer's operating instructions for all other spectrophotometer parameters.

7.6 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.7 Inject a measured uL aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.8 Either (1) run a series of silver standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus abosrbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.9 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.10 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased samples must be appropriately qualified.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a calibration blank and three standards. A calibration curve must be prepared each day.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one reagent blank per sample batch or every 20 samples to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared quality control reference sample every 10 samples.

8.6 Run one spiked replicate sample for every 10 samples or per analytical batch, whichever is more frequent. A replicate sample is a sample brought through the entire sample preparation process.

8.7 Duplicates, spiked samples, and check standards should be routinely analyzed. Refer to Chapter One for the proper protocol.

8.8 The method of standard additions (see Method 7000, Step 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 272.2 of Methods for Chemical Analysis of Water and Wastes.

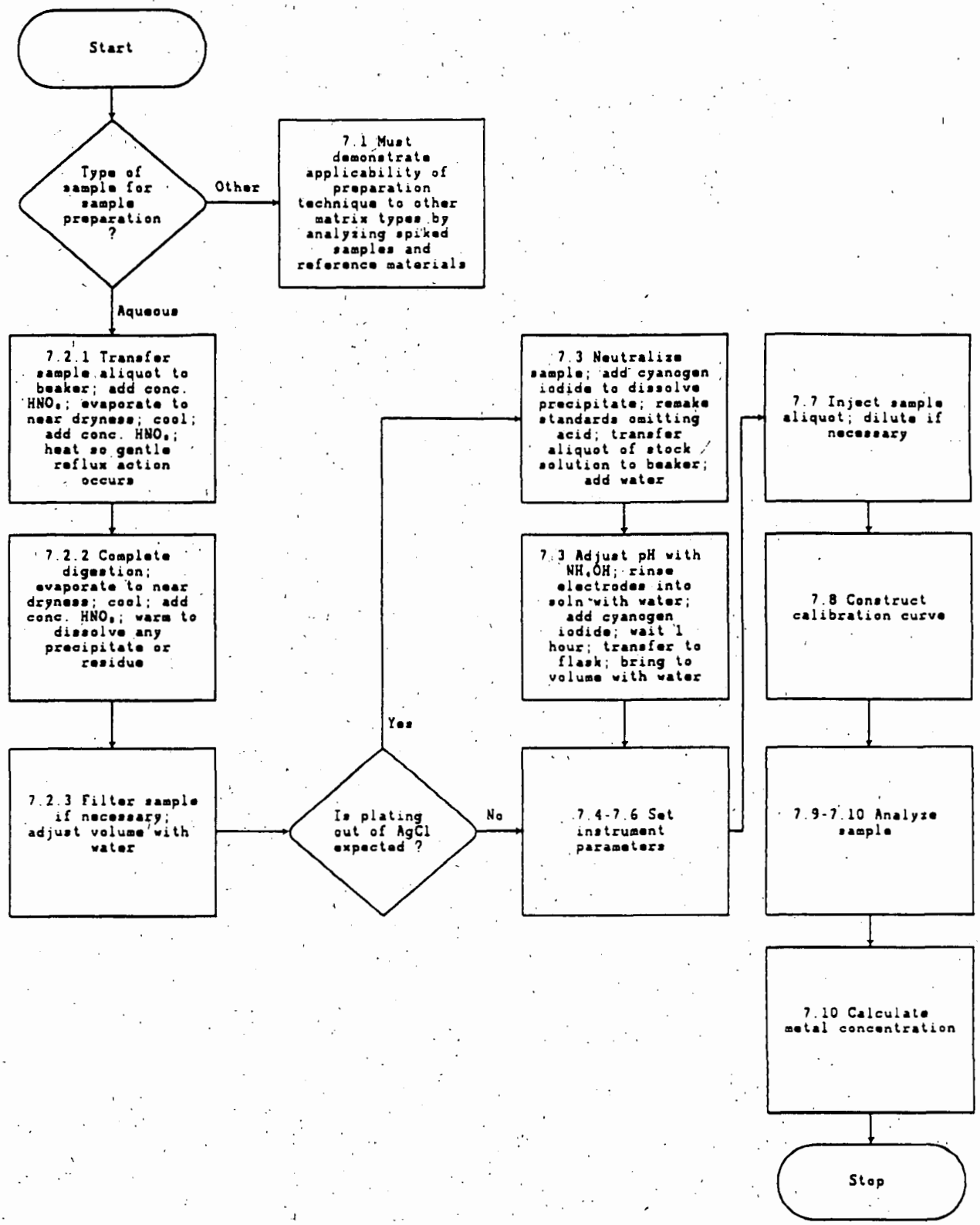
9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 1-25 ug/L.
Detection limit: 0.2 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.

METHOD 7761
SILVER (ATOMIC ABSORPTION, FURNACE TECHNIQUE)



METHOD 7780

STRONTIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000.

3.2 Chemical interference caused by silicon, aluminum, and phosphate are controlled by adding lanthanum chloride. Potassium chloride is added to suppress the ionization of strontium. All samples and standards should contain 1 mL of lanthanum chloride/potassium chloride solution (Step 5.3) per 10 mL of solution.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Strontium hollow cathode lamp.

4.2.2 Wavelength: 460.7 nm.

4.2.3 Fuel: Acetylene.

4.2.4 Oxidant: Air.

4.2.5 Type of flame: Oxidizing (fuel lean).

4.2.6 Background correction: not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards

5.2.1 Stock solution: (1.0 mL = 1.0 mg Sr). Dissolve 2.415 g of strontium nitrate, $Sr(NO_3)_2$, in 10 mL of concentrated HCl and 700 mL of water. Dilute to 1 liter with water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid as the samples and cover the range of expected concentrations in the samples. Calibration standards should also contain 1 mL of lanthanum chloride/potassium chloride solution per 10 mL.

5.3 Lanthanum Chloride/Potassium Chloride Solution. Dissolve 11.73 g of lanthanum oxide, La_2O_3, in a minimum amount of concentrated hydrochloric acid (approximately 50 mL). Add 1.91 g of potassium chloride, KCl. Allow solution to cool to room temperature and dilute to 100 mL with water.

CAUTION: REACTION IS VIOLENT! Add acid slowly and in small portions to control the reaction rate upon mixing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Step 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation - The procedures for preparation of the sample are given in Chapter Three, Step 3.2.

7.2 See Method 7000, Step 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.3 - 5 mg/L at a wavelength of 460.7 nm.
Sensitivity: 0.15 mg/L.
Detection limit: 0.03 mg/L.

9.1.1 Recoveries of known amounts of strontium in a series of prepared standards were as given in Table 1.

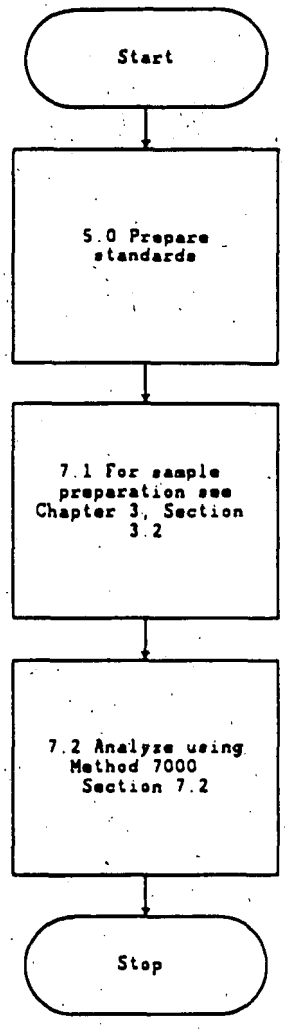
10.0 REFERENCES

1. Annual Book of ASTM Standards; ASTM: Philadelphia, PA, 1983; D3920.

TABLE 1.
RECOVERY

Amount added, mg/L	Amount found, mg/L	Bias	% Bias	Significant (95 % confidence level)
		Reagent Water Type II		
1.00	0.998	-0.002	-0.2	no
0.50	0.503	+0.003	+0.6	no
0.10	0.102	+0.002	+2	no
		Water of Choice		
1.00	1.03	+0.03	+ 3	no
0.50	0.504	+0.004	+ 0.8	no
0.10	0.086	-0.014	-14	no

Reference: Annual Book of ASTM Standards; ASTM: Philadelphia, PA, 1983; D3920.


Start
5.0 Prepare standards
7.1 For sample preparation see Chapter 3, Section 3.2
7.2 Analyze using Method 7000 Section 7.2
Stop

METHOD 7951

ZINC (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000.

3.2 Background correction should be used.

3.3 Zinc is a universal contaminant. Because of this and the high sensitivity of this method, great care should be taken to avoid contamination.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Drying time and temp: 30 sec at 125°C.

4.2.2 Ashing time and temp: 30 sec at 400°C.

4.2.3 Atomizing time and temp: 10 sec at 2500°C.

4.2.4 Purge gas: Argon or nitrogen.

4.2.5 Wavelength: 213.9 nm.

4.2.6 Background correction: Required.

4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower

atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards

5.2.1 Stock solution - Dissolve 1.000 g zinc metal (analytical reagent grade) in 10 mL of concentrated nitric acid and dilute to 1 liter with water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Step 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample Preparation - The procedures for preparation of the sample are given in Chapter Three, Step 3.2.

7.2 See Method 7000, Step 7.3, Furnace Technique.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are not available at this time.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.2-4 ug/L.
Detection limit: 0.05 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.

METHOD 7951
ZINC (ATOMIC ABSORPTION, FURNACE TECHNIQUE)