SAMPLING AND ANALYSIS PROCEDURES FOR SCREENING OF INDUSTRIAL EFFLUENTS FOR PRIORITY POLLUTANTS

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
EFFLUENT GUIDELINES DIVISION
WASHINGTON, D.C.

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FOREWORD

These guidelines for sampling and analysis of industrial wastes have been prepared by the staff of the Environmental Monitoring and Support Laboratory, at the request of the Effluent Guidelines Division, Office of Water and Hazardous Wastes, and with the cooperation of the Environmental Research Laboratory, Athens, Georgia. The procedures represent the current state-of-the-art but improvements are anticipated as more experience with a wide variety of industrial wastes is obtained. Users of these methods are encouraged to identify problems encountered and assist in updating the test procedures by contacting the Environmental Monitoring and Support Laboratory, EPA, Cincinnati, Ohio 45268.

CONTENTS

LIST OF TABLES

Appendices

I. General Information

II. Possible Sources for Some Priority Pollutant Standards

III. Collection of Samples for Screening Analyses

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

SUBJECT: Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants

DATE: MAY 27 1977

FROM: William A. Telliard, Chief
Energy and Mining Branch

TO: Project Officers
Effluent Guidelines Division

THRU: Robert B. Schaffer, Director
Effluent Guidelines Division

As you know, in the settlement of several cases in the District Court for the District of Columbia, the Environmental Protection Agency has agreed to review and revise regulations based on the Best Available Technology Economically Achievable (BAT), New Source Performance Standards, and Pretreatment Standards for 21 industrial categories.

In this revision, consideration is to be given to the application of limitations of a list of 65 materials appearing in Appendix A of the Settlement Agreement. These materials are generally referred to as priority pollutants. The priority pollutants are both single compounds and families of compounds. The Agency has established an unambiguous list of 129 compounds which it believes fulfills the requirements of the court order and can be analytically determined.

To maintain consistant sampling and analytical procedures the Agency has developed a sampling protocol and analytical methods to be used for screening for priority pollutants. This protocol represents the most current procedures for the sampling and analysis of these priority pollutants. Because of the large number of analysis required, argon plasma atomic-emission spectroscopy will be used by the Agency for most metals analysis. Pertinent information about this analytical method, which is an accepted alternate method under section 304(g) is attached.

The data gathering process basic to revising the regulations consists of two phases. The initial phase is the screening sampling and analysis procedure to ascertain the presence or

absence of the priority pollutants. The second phase or verification sampling will be used to quantify those pollutants found to be present during the screen sampling.

These materials are made available for your information and use during the screening phase only.

UNITED S..ATES ENVIRONMENTAL PROTECTIC.. AGENCY

SUBJECT: Approval of Alternate Test Procedure - Automated Simultaneous Analysis of Twenty Selected Elements by Inductively Coupled Argon Plasma Emission Spectroscopy

DATE: JAN 22 1976

FROM: Mr. Francis T. Mayo
Regional Administrator, Region V

TO: Mr. Thomas E. Yeates, Director
Central Regional Laboratory, Region V

THRU: Mr. Chris Timm, Director
Surveillance & Analysis Division, Region V

The Environmental Monitoring and Support Laboratory (EMSL) - Cincinnati, EPA has carefully reviewed your application for use of an alternate test procedure for the automated simultaneous analysis of twenty elements by emission spectroscopy using the inductively coupled argon plasma as the emission source. Your application specifies that the automated instrumental methodology will be used at the Central Regional Laboratory, Region V for all sample types applicable to the National Pollutant Discharge Elimination System (NPDES).

The proposed method uses the sample digestion procedure of 40 CFR Part 136, but instead of utilizing referee atomic absorption spectrometry, the digested sample is aspirated into a high temperature inductively coupled argon plasma (ICAP), and several total elemental concentrations in the aspirated sample are measured simultaneously using an emission spectrograph with an appropriate photomultiplier tube for each element. The calculation of the elemental concentrations is done by a computer interfaced to the spectrograph. Twenty elements, primarily metals, have been selected by the Central Regional Laboratory for analysis by ICAP-emission spectroscopy. In addition to total elemental concentrations, the proposed methodology can readily measure dissolved concentrations for the same elements simply by filtering a suitable aliquot through a 0.45 μ membrane, acidifying the filtrate as necessary for preservation, eliminating the digestion procedure and aspirating the filtrate into the ICAP-emission spectrograph.

The comparability data you have provided for ICAP-emission spectroscopy and referee atomic absorption spectrophotometry indicate the two methods yield equivalent data for a variety of waste effluents representative of the NPDES. ICAP-emission spectroscopy is shown to provide a comparable or superior performance, depending on the element, for the measurement of recovery and precision for random element "spikes" of NPDES waste effluents. Although the stated detection limits and lowest quantitatively determinable concentration vary slightly from day-to-day and are a function of the ICAP nebulizer, the reportable detection limits for ICAP-emission spectroscopy

Organics by Purge and Trap - Gas Chromatography

1. Scope

This method is designed to determine those "unambiguous priority pollutants," associated with the Consent Decree, that are amenable to the purge and trap method[1]. These compounds are listed in Table I of this section. It is a gas chromatographic-mass spectrometric (GC-MS) method intended for qualitative and semi-quantitative determination of these compounds during the survey phase of the industrial effluent study.

Certain compounds, acrolein and acrylonitrile, are not efficiently recovered by this method and should be determined by direct aqueous injection GC-MS. Direct aqueous injection GC-MS is recommended for all compounds that exceed 1000 µg/l.

The purge and trap and the liquid-liquid extraction methods are complementary to one another. There is an area of overlap between the two and some compounds may be recovered by either method. However, the efficiency of recovery depends on the vapor pressure and water solubility of the compounds involved. Generally, the area of overlap may be identified by compounds boiling between 130°C and 150°C with a water solubility of approximately two percent. When compounds are efficiently recovered by both methods, the chromatography determined the method of choice. The gas chromatographic conditions selected

for the purge and trap method are, generally, not suitable for the determination of compounds eluting later than chlorobenzene.

2. Special Apparatus and Materials

Sample extraction apparatus (minimum requirements):

5-ml glass syringes with Luer-Lok - 3 each

2-way syringe valves (Teflon or Kel-F) - 3 each

8-inch, 20 gauge syringe needle - 2 each

5-ml glass, gas-tight syringe, pressure-lok[a] or equivalent - 1 each

Tekmar Liquid Sample Concentrator, model LSC-1[b] or equivalent. Includes a sorbent trap consisting of 1/8 in. O.D. (0.09 to 0.105 in. I.D.) x 6 in. long stainless steel tube packed with 4 inches of Tenax-GC (60/80 mesh and 2 inches of Davison Type-15 silica gel (35/60 mesh).

3. Gas Chromatographic Column Materials

Stainless steel tubing 1/8 in. O.D. (0.09 to 0.105 in. I.D.) by 8 ft. long. Carbopack C (60/80 mesh) coated with 0.2% Carbowax 1500[c]. Chromosorb-W (60-80 mesh) coated with 3% Carbowax 1500.

(a) Available from Precision Sampling Corp., P.O. Box 15119, Baton Rouge, LA 70815.

(b) Available from Tekmar Company, P.O. Box 37202, Cincinnati, OH 45222.

(c) Available from Supelco, Supelco Park, Bellefonte, PA 16823. Stock No. 1-1826.

4. Procedure

Preparation of Standards - Prepare standard stock solutions (approximately 2 µg/µl) by adding, from a 100 µl syringe, 1 to 2 drops of the 99+% pure reference standard to methanol (9.8 ml) contained in a tared 10 ml volumetric flask (weighed to nearest 0.1 mg). Add the compound so that the two drops fall into the alcohol and do not contact the neck of the flask. Use the weight gain to calculate the concentration of the standard. Prepare gaseous standards, i.e., vinyl chloride, in a similar manner using a 5 ml valved gas-tight syringe with a 2 in. needle. Fill the syringe (5.0 ml) with the gaseous compound. Weigh the 10 ml volumetric flask containing 9.8 ml of methyl alcohol to 0.1 mg. Lower the syringe needle to about 5 mm above the methyl alcohol meniscus. Slowly inject the standard into the flask. The gas rapidly dissolves in the methyl alcohol. Reweigh the flask, dilute to volume, mix, tightly stopper, and store in a freezer. Such standards are generally stable for at least one week when maintained at less than 0°C. Stock standards of compounds which boil above room temperature are generally stable for at least four weeks when stored at 4°C.

[Safety Caution: Because of the toxicity of most organohalides, primary dilutions must be prepared in a hood. Further, it is advisable to use an approved respirator when handling high concentration of such materials.]

From the primary dilution prepare a secondary dilution mixture in methyl alcohol so that 20.0 µl of the standard, diluted to 100.0 ml in organic free water, will give a standard which produces a response close to that of the unknown. Also prepare a complex test mixture at a concentration of 100 ng/µl containing each of the compounds to be determined. Prepare a 20 µg/l quality check sample from the 100 ng/µl standard by dosing 20.0 µl into 100.0 ml of organic free water.

Internal Standard Dosing Solution - From stock standard solutions prepared as above, add a volume to give 1000 µg each of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane to 45 ml of organic free (blank water) contained in a 50 ml volumetric flask, mix and dilute to volume. Prepare a fresh internal standard on a weekly basis. Dose the internal standard mixture into every sample and reference standard analyzed.

Preliminary Treatment of Sample - Remove samples from cold storage (approximately an hour prior to analysis) and bring to room temperature by placing in a warm water bath at 20-25°C.

Purging and Trapping Procedure - Adjust the helium purge gas flow to 40 ml/min. Set the Tekmar 2-way valve to the purge position and open the purging device inlet. Remove the plungers from two 5-ml syringes and attach a closed 2-way syringe valve to each. Open the sample bottle and carefully

pour the sample into one of the syringes until it overflows. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while carefully adjusting the volume to 5.0 ml. Then close the valve. Fill the second syringe in an identical manner from the same sample bottle. Use the second syringe for a duplicate analysis as needed. Open the syringe valve and introduce 5.0 µl of the internal standard mixture through the valve bore, then close the valve. Attach the 8-inch needle to the syringe valve and inject the sample into the purging device. Seal the purging device and purge the sample for 12 minutes. The purged organics are sorbed on the Tenax-silica gel trap at room temperature (20-25°C).

While the sample is being purged, cool the gas chromatographic column oven to near room temperature (20-30°C). To do this, turn heater off and open column oven door.

At the completion of the 12-minute purge time, inject the sample into the gas chromatograph by turning the valve to the desorb position. Hold in this position for four minutes while rapidly heating the trap oven to 180°C, then return the valve to the purge position, close the GC column oven door, and rapidly heat the GC oven to 60°C. Consider this time zero and begin to collect retention data. Hold at 60°C for four minutes, then program at 8°/minute to 170°C and hold until all compounds have eluted. Begin collecting GC-MS

GC-MS data as soon as the GC-MS vacuum system has stabilized ($<10^{-5}$ torr).

While the sample is being chromatographed, flush the purging device with two 5-ml volumes of organic free water. Then bake out the trap (vent to atmosphere) to minimize the amount of water desorbed into the GC-MS system during the succeeding injection step. [Note: If this bake out step is omitted, the amount of water entering the GC-MS system will progressively increase causing deterioration of and potential shut down of the system.]

GC-MS Determination - Suggested analytical conditions for determination of the priority pollutants amenable to purge and trap, using the Tekmar LSC-1 and the computerized Finnigan 1015 GC-MS are given below. Operating conditions vary from one system to another; therefore, each analyst must optimize the conditions for his equipment.

Purge Parameters

Purge gas - Helium, high purity grade

Purge time - 12 minutes

Purge flow - 40 ml/min.

Trap dimensions - 1/8 in. O.D. (0.09 to 0.105 in. I.D.) x 6 in. long

Trap sorbent - Tenax-GC, 60/80 mesh (4 in.) plus Type 15 silica gel, 35/60 mesh (2 in.)

Desorption flow - 20 ml/min.

Desorption time - 4 min.

Desorption temperature - 180°C

Gas Chromatographic Parameters

Column - Stainless steel, 8 ft. long x 1/8 in. O.D. (0.09 to 0.105 in. I.D.) packed with Carbopack C (60/80 mesh) coated with 0.2% Carbowax 1500, preceded by a 1 ft. x 1/8 in. O.D. (0.09 to 0.105 in. I.D.) packed with Chromosorb-W coated with 3% Carbowax 1500.

Carrier gas - Helium at 33 ml/min.

Oven temperature - Room temperature during trap desorption, then rapidly heat to 60°C, hold at 60°C for four minutes, then program to 170°C at 8°/minute. Hold at 170°C for 12 minutes or until all compounds have eluted.

Mass Spectrometer Parameters

Data system - System Industries System 150

Separator - glass jet

Electron energy - 70 ev

Emission current - 500 ua

Ion energy - 6 volts

Lens voltage - (-)100 volts

Extractor voltage - 8 volts

Mass range - 20-27, 33-260 amu

Integration time/amu - 17 milliseconds

Samples/amu - 1

Gas Chromatographic Column Conditioning Procedure - Attach the Carbowax 1500-Chromosorb end of the column to the inlet system of the gas chromatograph. Do not, at this time,

attach the column exit to the detector. Adjust the helium flow rate through the column to 33 ml/minute. Allow the column to flush with helium for ten minutes at room temperature, then program the oven from room temperature to 190°C at 4°C/minute. Maintain the oven at 190°C overnight (16 hours).

Handle the column with extreme care once it has been conditioned because the Carbopack is fragile and easily fractured. Once fractured, active sites are exposed resulting in poor peak geometry (loss of theoretical plates). Reconditioning, generally, revitalizes the analytical column. Once properly conditioned, the precolumn may be removed. The retention data listed in Table I was collected with the precolumn in the system.

Quality Assurance - The analysis of blanks is most important in the purge and trap technique since the purging device and the trap can be contaminated by residues from very concentrated samples or by vapors in the laboratory. Prepare blanks by filling a sample bottle with low-organic water (blank water) that has been prepared by passing distilled water through a pretested activated carbon column. Blanks should be sealed, stored at 4°C, and analyzed with each group of samples.

After each sample analysis, thoroughly, flush the purging device with blank water and bake out the system. Subsequently, analyze a sample blank (one that has been transported

to and from the sampling site). If positive interferences are noted, analyze a fresh laboratory sample of blank water. If positive interference still occurs, repeat the laboratory blank analysis. If interference persists, dismantle the system, thoroughly, clean all parts that the sample, purge gas and carrier gas comes into contact with and replace or repack the sorbent trap and change purge and carrier gas.

Precision - Determine the precision of the method by dosing blank water with the compounds selected as internal standards - bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane - and running replicate analyses. These compounds represent early, middle, and late eluters over the range of the Consent Decree compounds and are not, themselves, included on the list. Construct Quality Control charts from the data obtained according to directions in Reference 9.

The sample matrix can affect the purging efficiencies of individual compounds; therefore, each sample must be dosed with the internal standards and analyzed in a manner identical to the internal standards in blank water. When the results of the dosed sample analyses show a deviation greater than two sigma, repeat the dosed sample analyses. If the deviation is again greater than two sigma, dose another aliquot of the same sample with the compounds of interest at approximately two times the measured values and analyze. Calculate the recovery for the individual compounds using these data.*

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*See Reporting of Data Section, p. 11.

Calibration of the gas chromatography-mass spectrometry (GC-MS) system - Evaluate the system performance each day that it is to be used for the analysis of samples or blanks. Inject a sample of 20 nanograms of decalfuorotriphenylphosphine[d] and plot the mass spectrum. The criteria in Reference 2 must be met and all plots from the performance evaluation, documented and retained as proof of valid performance.

Analyze the 20 µg/l standard to demonstrate instrument performance for these compounds.

Qualitative and Quantitative Determination - The characteristic masses or mass ranges listed in Table II of this section are used for qualitative and quantitative determination of volatile priority pollutants. They are used to obtain an extracted ion current profile (EICP)[e] for each compound. For very low concentrations, the same masses may be used for selected ion monitoring (SIM)[f]. The primary ions to be used to quantify each compound are also listed. If the sample produces an interference for the primary ion, use a secondary ion to quantify.

(d) Available from PCR, Inc., Gainesville, FL.

(e) EICP is the reduction of mass spectrometric data acquired by continuous, repetitive measurement of spectra by plotting the change in relative abundance of one or several ions as a function of time.

(f) SIM is the use of a mass spectrometer as a substance selective detector by measuring the mass spectrometric response at one or several characteristic masses in real time.

Quantify samples by comparing the area of a single mass (see Table II) of the unknown in a sample to that of a standard. When positive responses are observed, prepare and analyze a reference standard so that the standard response closely approximates the sample response. Calculate the concentration in the sample as follows:

$$\frac{\frac{(\text{Area for unknown})}{(\text{Area for standard})}}{\text{Concentration of standard } (\mu g/l)} = \mu g/l \text{ of unknown}$$

5. Reporting of Data

Report all results to two significant figures or to the nearest 10 µg/l. Report internal standard data to two significant figures.

As the analyses are completed, transfer GC-MS data to magnetic tape as described under reporting of data in method for "Organics by Liquid-Liquid Extraction - Gas Chromatography."

Report all quality control (QC) data along with the analytical results for the samples. In addition, forward all QC data to EMSL, Cincinnati.

6. Direct Aqueous Injection Gas Chromatography

As noted in the Scope, Acrolein and acrylonitrile should be analyzed by direct aqueous injection gas chromatography-mass spectrometry. See references (3), (4), and (5) for these methods. The detection level for these methods is 0.1 mg/l and above.

Table I

Elution Order of Volatile Priority Pollutants[a]

Compound	RRT[b]	Purging Efficiency (percent)	Purging Efficiency Modified Method (percent)
chloromethane	0.152	91	
dichlorodifluoromethane	0.172	0	100[c]
bromomethane	0.181	85	
vinyl chloride	0.186	101	
chloroethane	0.204	90	
methylene chloride	0.292	76	
trichlorofluoromethane	0.372	96	
1,1-dichloroethylene	0.380	97	
bromochloromethane(IS)	0.457	88	
1,1-dichloroethane	0.469	89	
trans-1,2-dichloroethylene	0.493	92	
chloroform	0.557	95	
1,2-dichloroethane	0.600	98	
1,1,1-trichloroethane	0.672	94	
carbon tetrachloride	0.684	87	
bromodichloromethane	0.750	92	
bis-chloromethyl ether[d]	0.760	0	
1,2-dichloropropane	0.818	92	
trans-1,3-dichloropropene	0.847	90	
trichloroethylene	0.867	89	
dibromochloromethane	0.931	87	
cis-1,3-dichloropropene	0.913	85	
1,1,2-trichloroethane	0.913	88	
benzene	0.937	no data	
2-chloroethylvinyl ether	0.992	no data	
2-bromo-1-chloropropane(IS)	1.000	92	
bromoform	1.115	71	
1,1,2,2-tetrachloroethene	1.262	88	
1,1,2,2-tetrachloroethane	1.281	58	

Table I (cont'd)

Compound	RRT[b]	Purging Efficiency (percent)	Purging Efficiency Modified Method (percent)
1,4-dichlorobutane(IS)	1.312	74	
toluene	1.341	no data	
chlorobenzene	1.489	89	
ethylbenzene	1.814	no data	
acrolein	unknown	12	74[e]
acrylonitrile	unknown	no data	

(a) These data were obtained under the following conditions: GC column - stainless steel, 8 ft. long x 0.1 in. I.D. packed with Carbopack C (60/80 mesh), coated with 0.2% Carbowax 1500; preceeded by a 1 ft. long x 0.1 in. I.D. column packed with Chromosorb W coated with 3% Carbowax 1500; carrier flow - 40 ml/min.; oven temperature - initial 60°C held for 3 min., programmed 8°C/min. to 160°C and held until all compounds eluted. The purge and trap system used was constructed by EPA. Under optimized conditions, commercial systems will provide equivalent results.

(b) Retention times relative to 2-bromo-1-chloropropane with an absolute retention time of 829 seconds.

(c) No measurable recovery using standard purging and trapping conditions. Under modified conditions, i.e., purging at 10 ml/min. for 12 min., recovery is 100%.

(d) Bis-chloromethyl ether has a very short half-life in water and is not likely to be detected in water.

(e) Recovery 12% under standard purging conditions, i.e., room temperature, 30% at 55°C, and 74% at 95°C.

Table II

Characteristic Ions of Volatile Organics

Compound	EI Ions (Relative intensity)	Ion used to quantify
chloromethane	50(100); 52(33)	50
dichlorodifluoromethane	85(100); 87(33); 101(13); 103(9)	101
bromomethane	94(100); 96(94)	94
vinyl chloride	62(100); 64(33)	62
chloroethane	64(100); 66(33)	64
methylene chloride	49(100); 51(33); 84(86); 86(55)	84
trichlorofluoromethane	101(100); 103(66)	101
1,1-dichloroethylene	61(100); 96(80); 98(53)	96
bromochloromethane(IS)	49(100); 130(88); 128(70); 51(33)	128
1,1-dichloroethane	63(100); 65(33); 83(13); 85(8); 98(7); 100(4)	63
trans-1,2-dichloroethylene	61(100); 96(90); 98(57)	96
chloroform	83(100); 85(66)	83
1,2-dichloroethane	62(100); 64(33); 98(23); 100(15)	98
1,1,1-trichloroethane	98(100); 99(66); 117(17); 119(16)	97
carbon tetrachloride	117(100); 119(96); 121(30)	117
bromodichloromethane	83(100); 85(66); 127(13); 129(17)	127
bis-chloromethyl ether	79(100); 81(33)	79
1,2-dichloropropane	63(100); 65(33); 112(4); 114(3)	112
trans-1,3-dichloropropene	75(100): 77(33)	75
trichloroethylene	95(100); 97(66); 130(90); 132(85)	130
dibromochloromethane	129(100); 127(78); 208(13); 206(10)	127
cis-1,3-dichloropropene	75(100); 77(33)	75

Table (cont'd)

Compound	EI Ions (Relative intensity)	Ion used to quantify
1,1,2-trichloroethane	83(95); 85(60); 97(100); 99(63); 132(9); 134(8)	97
benzene	78(100)	78
2-chloroethylvinyl ether	63(95); 65(32); 106(18)	106
2-bromo-1-chloropropane(IS)	77(100); 79(33);156(5)	77
bromoform	171(50);173(100); 175(50); 250(4); 252(11); 254(11); 256(4)	173
1,1,2,2-tetrachloroethene	129(64); 131(62); 164(78); 166(100)	164
1,1,2,2-tetrachloroethane	83(100); 85(66); 131(7); 133(7); 166(5); 168(6)	168
1,4-dichlorobutane(IS)	55(100); 90(30); 92(10)	55
toluene	91(100); 92(78)	92
chlorobenzene	112(100); 114(33)	112
ethylbenzene	91(100); 106(33)	106
acrolein	26(49); 27(100); 55(64); 56(83)	56
acrylonitrile	26(100); 51(32); 52(75); 53(99)	53

Organics by Liquid-Liquid Extraction -
Gas Chromatography

1. Scope

This method is designed to determine those "unambiguous priority pollutants" associated with the Consent Decree, that are solvent extractable and amenable to gas chromatography. These compounds are listed in Tables III to V of this section. Except for the pesticides, it is a gas chromatographic-mass spectrometric method intended for qualitative and semi-quantitative determination of these compounds during the survey phase of the industrial effluent study. Pesticides are initially determined by electron capture-gas chromatography and, qualitatively, confirmed by mass spectrometry.

2. Special Apparatus and Materials

Separatory funnels - 2 and 4-liter with Teflon stopcock

Continuous liquid-liquid extractors - any such apparatus designed for use with solvents heavier than water and having a capacity of 2 to 5-liters[(a)]. Connecting joints and stopcocks must be of Teflon or glass with no lubrication.

3. Procedure

Sample Preparation for GC-MS Survey - Blend the composite sample to provide a homogeneous mixture including

(a) Available from Aldrich Chemical Co., Milwaukee, WI, Catalog No. Z10, 157-5.

a representative portion of the suspended solids that are present. No specific method is required but a motor driven mechanical stirrer with a propeller type blade is suggested. Stirring with metal devices is acceptable for organic sampling.

Transfer the sample from the composite container through a glass funnel into a 2-liter graduated cylinder and measure the volume. Then transfer to a 4-liter separatory funnel or a continuous extractor as described below. Rinse the cylinder with several portions of the first volume of extracting solvent. Note: [Either separatory funnel or continuous extraction is acceptable for isolation of the organics. Continuous extraction must be used when emulsions cannot be broken. See discussion under Emulsions.]

Base-Neutral Extraction

Separatory Funnel Extraction - Adjust the pH of the sample with 6 N NaOH to 11 or greater. Use multirange pH paper for the measurement. Serially extract with 250 x 100 x 100 ml portions of distilled-in-glass methylene chloride. (About 40 ml of the first 250 ml portion will dissolve in the sample and not be recovered.) Shake each extract for at least 2 min by the clock.

Dry and filter the solvent extract by passing it through a short column of sodium sulfate. Concentrate the solvent by Kuderna-Danish (K-D) evaporation (distillation). The sodium sulfate should be prewashed in the column with methylene

chloride. [Note: Check sodium sulfate blank and, if necessary, heat in an oven at 500°C for 2 hours to remove interfering organics.] After drying the extract, rinse the sodium sulfate with solvent and add to the extract.

Evaporate the extract to 5-10 ml in a 500 ml K-D apparatus fitted with a 3-ball macro-Snyder column and a 10 ml calibrated receiver tube. Allow the K-D to cool to room temperature. Remove the receiver, add fresh boiling chips, attach a two-chamber micro-Snyder column and carefully evaporate to 1.0 ml or when active distillation ceases. Remove the micro-Snyder column and carefully evaporate to 1.0 ml or when active distillation ceases. Remove the micro-Snyder column and add the internal standard: 10 µl of 2 µg/µl d_{10}-anthracene (per each ml of extract). Mix thoroughly.

If it is to be overnight or longer before the extract is run by GC-MS, transfer it from the K-D ampul with a disposable pipet to a solvent tight container. The recommended container is a standard 2 ml serum vial with a crimp cap lined with Teflon coated rubber. These are inert and methylene chloride can be held without evaporation loss for months if caps are unpierced. When the extracts are not being used for analysis, store them with unpierced caps in the dark and at refrigerator or freezer temperatures.

Acid (Phenols) Extraction - Adjust the pH of the base-neutral extracted water with 6 N HCl to 2 or less. Serially

extract with 200 x 100 x 100 ml portions of distilled-in-glass methylene chloride. (Note that only 200 ml is used for the first extraction). Proceed as described for the base-neutral extract, including the addition of the internal standard.

Emulsions - The recovery of 85% of the added solvent will constitute a working definition of a broken emulsion. (You may correct the recovery of the first portion for water solubility of methylene chloride.) Any technique that meets this criteria is acceptable. Among techniques that have been tried on these samples with fair success are:

1. Centrifugation of the emulsion layer after removel of any separated solvent.
2. Passage of the emulsion through a column plugged with a ball of methylene chloride-wet glass wool. The solvent used to wet the wool and to wash it after the emulsion goes through must be measured and subtracted from the total volume to determine 85% recovery.
3. Relative to labor, solvent is cheap. The addition of excess solvent sometimes breaks weak emulsions. You must remember to use excess solvent in the blanks also.
4. Let the emulsion stand for up to 24 hrs.
5. Draw off the small amount of free solvent that separates and slowly drip it back in the top of the

separatory funnel and through the sample and emulsion.

Other ideas include stirring with a glass rod, heating on a steam bath, addition of concentrated sodium sulfate solution, and sonication. See discussion in Appendix I.

Continuous Extraction - If you cannot achieve 85% solvent recovery, start with a fresh aliquot of sample and extract by continuous extraction.

Adjust the pH of the sample as appropriate, pour into the extractor, and extract for 24 hours. When extracting a 2-liter sample, using the suggested equipment, two liters of blank water must be added to provide proper solvent recycle.

For operation, place 200-300 ml of solvent in the extractor before the sample is added and charge the distilling flask with 500 ml of solvent. At the end of the extraction remove the solvent from the distilling flask only and evaporate and treat as described in the base-neutral extract section.

Blank Extraction: It is not entirely certain that 2 liters of blank will always be available. When it is, proceed to process it as the corresponding sample was done. Include any emulsion breaking steps that used glass wool, excess solvent or additional chemicals. If less than 2 liters is available, measure the blank and bring it to volume with distilled water. On analysis make the necessary quantitative corrections.

Pesticides: These compounds are to be analyzed by EC-GC using the EPA method published in the Federal Register, Vol. 38, Number 125, Part II, pp. 17318-17323. (Friday, June 29, 1973). One-liter rather than 100 ml is to be extracted. The solvent amounts given in the method and other parameters remain unchanged. If pesticides are found by EC, the extract is to be carefully evaporated (clean airstream) to 0.5 ml and sent for GC-MS confirmation.

The compounds to be analyzed by EC-GC are listed in Table III.

If the pesticide sample has been received in a 1-gal. bottle, hand shake the bottle for 1 min. by the clock to evenly suspend sediment. Pour the sample into a 1-liter graduated cylinder and measure the volume. Then transfer the sample to a 2-liter separatory funnel and rinse the cylinder with the first volume of extracting solvent. Use additional small volumes of solvent if necessary to transfer all of the sample. Proceed with the extraction using the solvents and amounts prescribed in the published method.

If the sample is to be taken from the original composite bottle, homogeneously mix as described earlier and transfer a 1-liter aliquot to a graduated cylinder, then transfer to the separatory funnel with the aid of a glass funnel and rinse the cylinder as above.

If intractable emulsions are encountered that cannot be broken as described in the GC-MS survey section, then a fresh 1-liter sample should be processed in a continuous extractor using methylene chloride as the solvent as described earlier. The methylene chloride will have to be evaporated to a small volume and exchanged into hexane for clean-up or EC-GC analysis. To do this, evaporate the methylene chloride to 6 to 8 ml, cool, add 20 ml of hexane and a fresh boiling stone and re-evaporate to the desired analytical volume (5 ml or less).

Final storage and transport of sample extracts: After analysis, the extracts of the base-neutrals, acids, blanks and pesticides are to be sent to ERL, Athens, GA 30601, ATTN: Dr. Walter Shackelford.

Each extract is to be washed out of its container into a 10 ml glass ampul and brought to 5 ml ± 1 ml. Methylene chloride is the solvent for the base-neutrals and acids, hexane for pesticides. The ampuls are to be sealed in a rounded-off, fire polished manner, i.e., no thin sharp peaks of glass that are easily broken on handling and shipping. After sealing the ampuls, put an indelible mark at the solvent level. Securely attach a label or tag that gives:

Type of fraction (base-neutral, etc.)

Industrial category

Name (of plant, city and state)

Specific source or stage of treatment

Date sampled originally

Date sealed

Name of contractor and analytical laboratory

Wrap the ampuls in packing material to prevent breakage and mail or ship them postpaid at ambient temperature. When the samples are safely in ampuls, the remainder of the composite sample may be discarded.

4. GC-MS Analysis

Compounds to be analyzed by GC-MS alone fall into two categories--those in the base-neutral extract (Table IV) and those in the acid extract (Table V). Pesticides (Table III that were tentatively identified in the pesticide analysis will be confirmed by GC-MS.

The base-neutral extractables may be separated and eluted into the MS under the following chromatographic conditions:

Column - 6 foot, 2.0 mm inside diameter, glass

Packing - 1% SP2250 on 100/120 mesh Supelcoport

Program - hold 4 minutes @ 50°, program 50°-260°
@ 8°/min., hold 20 minutes @260°

Injector - 275°

Separator - 275°

Carrier gas - He @ 30 ml/min

Injection size - $\geq$2 µl

Table IV lists the 49 base-neutral extractable compounds in order of relative retention times (compared to hexachlorobenzene) for the above GC conditions. Detection limits were determined by MS response. The seven compounds without retention times or limits of detection were not available for this report. It is not recommended that 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) be acquired due to its extreme toxicity. Based on their similarity to compounds that were available all seven are expected to be chromatographable using these standard conditions. In addition the characteristic masses recommended for MS identification are listed in Table IV.

The limits of detection given in Tables III and IV refer to the quantity necessary to inject to get confirmation by the MS methods described below.

At the beginning of each GC-MS run of a base-neutral extract, the operator should demonstrate the ability to chromatograph benzidine at the 40 ng level. Only after this is accomplished should the run be started. If benzidine can be chromatographed, the other nitrogen-containing compounds of Table IV can be chromatographed as well.

If desired, capillary or SCOT columns may be used instead of the packed column of SP-2250. Coatings of OV-17 or SP-2250 may be used. The elution order of OV-17 and SP-2250 are very similar. Some specific data for OV-17 is given in Table VII. The performance criteria for benzidine must still be met

and in addition, the system must be shown to elute the late running polynuclear aromatic compounds.

The acid extractables may be chromatographed as follows:

Column, 6 foot, 2.0 mm inside diameter, glass

Packing - Tenax GC, 60/80 mesh

Program - 180° - 300° @ 8°/min

Injector - 290°

Separator - 290°

Carrier Gas - He @ 30 ml/min

Injection size - $\geq$2 µl

Table V lists the 11 acid extractables in order of relative retention times (compared to 2-nitrophenol). Chromatography of nitrophenols is poor. The limits of detection given refer to the amounts required to get MS confirmation by the methods described below. See Appendix I.

Before an acid extract is run on the GC-MS the operator should demonstrate the ability to detect 100 ng of pentachlorophenol.

Mass Spectrometry should be conducted with a system utilizing a jet separator for the GC effluent since membrane separators lose sensitivity for light molecules and glass frit separators inhibit the elution of polynuclear aromatics. A computer system should be interfaced to the mass spectrometer to allow acquisition of continuous mass scans for the duration of the chromatographic program. The computer system

should also be equipped with mass storage devices for saving all data from GC-MS runs. There should be computer software available to allow searching any GC-MS run for specific ions and plotting the intensity of the ions with respect to time or scan number. The ability to integrate the area under any specific ion plot peak is essential for quantification.

To indicate the presence of a compound by GC-MS, three conditions must be met. First, the characteristic ions for the compound (Tables III-V) must be found to maximize in the same spectrum. Second, the time at which the peak occurs must be within a window of ± 1 minute for the retention time of this compound. Finally, the ratios of the three peak heights must agree with the relative intensities given in Tables III-V within ± 20%.

An example of identifying a component is as follows:

It is known that hexachlorobenzene elutes from the SP2250 column at 19.4 minutes. Hexachlorobenzene has characteristic mass ions at 284(100%), 142(30%), and 249(24%). The computer is asked to display a plot of the intensities of these ions versus time (or MS scan number) and the window from 18.4-20.4 minutes is examined for the simultaneous peaking of the intensities of these ions. If all three ions are present, the ratio of the peak heights is checked to verify that it is 100:30:24 ± 20%. If the three tests are successful, hexachlorobenzene has been identified in the sample.

Table III lists the 18 pesticides and PCB's that will be confirmed by GC-MS using the SP2250 column. Chlordane, toxaphene and the PCB's have retention ranges rather than specific times due to their being multicomponent mixtures. It is suggested that the first 14 materials be confirmed exactly as the other base-neutral compounds.

The last four materials require special treatments. Chlordane is expected to produce two main peaks within the retention range given in which all three masses listed will maximize. Toxaphene will produce several (5-15) peaks in which the masses given will maximize within the retention time range. For the PCB's each mass given corresponds to the molecular ion of PCB isomers, e.g., 294 is tetrachlorobiphenyl. A specific mass plot will show multiple peaks for each of these ions within the retention time listed, but in general they will not maximize in the same TIC peak. For these four materials in particular it is necessary to also run a standard. Because GC-MS is only being used for confirmation--and at its limit of detection--all quantification will be done by EC-GC for the pesticides. The methods for these four are not final and feedback from the field to Dr. Shackelford is welcome.

When a compound has been identified, the quantification of that compound will be based on the integrated area from the specific ion plot of the first listed characteristic ion in Tables IV and V. Quantification will be done by the internal standard method using deuterated anthracene. Response

factors, therefore, must be calculated to compare the MS response for known quantities of each priority pollutant with that of the internal standard. The response ratio (R) may be calculated as:

$$R = \frac{Ac}{Aa} \times \frac{Ca}{Cc}$$

where Ac is the integrated area of the characteristic ion from the specific ion plot for a known concentration, Cc. Aa and Ca are the corresponding values for deuterated anthracene. The relative response ratio for the priority pollutants should be known for at least two concentration values--40 ng to approximate 10 ppb and 400 ng to approximate the 100 ppb level. Those compounds that do not respond at either of these levels may be run at concentrations appropriate to their response. For guidance in MS limits of detection refer to the values given in Tables III-V.

The concentration of a compound in the extract may now be calculated using:

$$C = \frac{Ac \times Ca}{Aa \times R}$$

where C is the concentration of a component, Ac is the integrated area of the characteristic ion from the specific ion plot, R is the response ratio for this component, Aa is the integrated area of the characteristic ion in the specific ion plot for deuterated anthracene, and Ca is the concentration of deuterated anthracene in the injected extract.

In samples that contain an inordinate number of interferences the chemical ionization (CI) mass spectrum may make identification easier. In Tables IV and V characteristic CI ions for most compounds are given. The use of chemical ionization MS to support EI is encouraged but not required.

5. Quality Assurance

GC-MS system performance evaluation is required each day the system is used for samples or reagent blanks. A sample of 20 ng of decafluorotriphenylphosphine[b] is injected into the system and the mass spectrum is acquired and plotted. Criteria established in Reference 2 must be met. The analyst must also demonstrate that the analytical conditions employed result in sharp total ion current peaks for 40 ng of benzidine on the SP2250 column when this column is used and 100 ng of pentachlorophenol on the Tenax GC column when it is used with the MS as a detector. All plots from the performance evaluation must be retained as proof of valid performance.

As performance evaluation samples become available from EMSL-Cincinnati, they are to be analyzed by solvent extraction once each 20 working days and the results reported with other analytical data.

The 1% SP2250 and Tenax GC column packings are available by request to EPA contractors from Dr. Walter Shackelford, EPA, Athens, GA.

(b) Available from PCR, Gainesville, FL

Standards for the priority pollutants may be obtained from the sources listed in Appendix II*. Those compounds marked with an asterisk have not yet been received by the Athens laboratory.

In order to minimize unnecessary GC-MS analysis of blanks, the extract may be run on a FID-GC equipped with appropriate SP2250 and Tenax GC columns. If no peaks are seen of intensities equal to or greater than the deuterated anthracene internal standard, then it is not necessary to do a GC-MS analysis. If such peaks are seen, then the blank must be sent for full priority pollutant analysis.

The contractor will look for all priority pollutants to the limit of 10 µg/l except in those cases listed in Tables IV-V in which limits of detection are too high for analysis at this level.

6. Reporting of Data

All concentrations should be reported in ranges--10 ppb, 100 ppb, and greater than 100 ppb. Report concentrations for pesticides as prescribed in the Federal Register Method. The relative response ratios from MS analysis should be included when reporting data.

All GC-MS data is to be saved on 9-track magnetic tape and sent to the Athens Environmental Research Laboratory for storage and later evaluation. The tape format is:

*Those labs which are under contract to perform GC-MS analyzes for EPA, may obtain a set of standards from Mr. William Telliard, Chief, Energy and Mining Branch, (202) 426-2726.

Type - 9 track, 800 BPI, 2400 foot reels

Record length - 80

Block Size - $\leq$4000 (specify)

Code - EBCDIC

An acceptable data format would have the first two records containing the sample identification. Subsequent records contain eight mass-intensity pairs, each of which is 10 characters long. Each mass and each intensity is 5 characters long and left justified. At the end of each spectrum in a sample run, the last mass-intensity pair is blank to denote the end of the spectrum. When all data for the run is on the tape, an end-of-file mark should be written. The next sample run can then be entered. One example is:

2 Records:Sample 1 identification

N Records:Spectrum 1 of sample, last mass-intensity pair is blank to denote end of spectrum

M Records:Spectrum 2 of sample, last mass-intensity pair is blank to denote end of spectrum

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L Records:Spectrum N of sample, last mass-intensity pair is blank to denote end of spectrum

END OF FILE

2 Records:Sample 2 identification

etc.

Other data formats are possible, but any format that is used must be accompanied by a full explanation of all record formats.

All magnetic tapes, documentation and a table of MS response ratios should be sent to:

Dr. W. M. Shackelford
Athens Environmental Research Laboratory
College Station Road
Athens, GA 30601

Table III. Pesticides

Compound Name	RRT[1] (hexachlorobenzene)	Detection Limit (ng)	Characteristic EI ions (Rel. Int.)
β-endosulfan	0.51	40	201(100), 283(48), 278(30)
α-BHC	1.02	40	183(100), 109(86), 181(91)
γ-BHC	1.09	40	183(100), 109(86), 181(91)
β-BHC	1.12	40	181(100), 183(93), 109(62)
aldrin	1.14	40	66(100), 220(11), 263(73)
heptachlor	1.15	40	100(100), 272(60), 274(46)
heptachlor epoxide	1.23	40	355(100), 353(79), 351(60)
α-endosulfan	1.24	40	201(100), 283(48), 278(30)
dieldrin	1.28	40	79(100), 263(28), 279(22)
4,4'-DDE	1.30	40	246(100), 248(64), 176(65)
4,4'-DDD	1.33	40	235(100), 237(76), 165(93)
4,4'-DDT	1.38	40	235(100), 237(72), 165(59)
endrin	1.41	40	81(100), 82(61), 263(70)
endosulfan sulfate	1.41	20	272(100), 387(75), 422(25)
δ-BHC			183(100), 109(86), 181(90)
chlordane	1.14-1.37		373(19), 375(17), 377(10)
toxaphene	1.22-1.47		(231, 233, 235)*
PCB-1242	0.93-1.24		(224, 260, 294)*
PCB-1254	1.18-1.41		(294, 330, 362)*

* These ions are listed without relative intensities since the mixtures they represent defy characterization by three masses.

** These three ions are characteristic for the α and γ forms of chlordane. No stock should be set in these three for other isomers.

[1] 1% SP-2250 on 100/120 mesh Supelcoport in a 6' x 2 mm id glass column; He @ 30 ml/min; Program: 50° for 4 min, then 8°/min to 260° and hold for 15 min.

Table IV. Base-neutral Extractables

Compound Name	RRT[1] (hexachloro-benzene)	Limit of Detection (ng)	Characteristic EI ions (Rel. Int.)	CI ions (Methane)
1,3-dichlorobenzene	0.35	40	146(100), 148(64), 113(12)	146, 148, 150
1,4-dichlorobenzene	0.36	40	146(100), 148(64), 113(11)	146, 148, 150
hexachloroethane	0.38	40	117(100), 199(61), 201(99)	199, 201, 203
1,2-dichlorobenzene	0.39	40	146(100), 148(64), 113(11)	146, 148, 150
bis(2-chloroisopropyl) ether	0.47	40	45(100), 77(19), 79(12)	77, 135, 137
hexachlorobutadiene	0.55	40	225(100, 223(63), 227(65)	223, 225, 227
1,2,4-trichlorobenzene	0.55	40	74(100), 109(80), 145(52)	181, 183, 209
naphthalene	0.57	40	128(100), 127(10), 129(11)	129, 157, 169
bis(2-chloroethyl)ether	0.61	40	93(100), 63(99), 95(31)	63, 107, 109
hexachlorocyclopentadiene	0.64	40	237(100), 235(63), 272(12)	235, 237, 239
nitrobenzene	0.64	40	77(100), 123(50), 65(15)	124, 152, 164
bis(2-chloroethoxy)methane	0.68	40	93(100), 95(32), 123(21)	65, 107, 137
2-chloronaphthalene	0.76	40	162(100), 164(32), 127(31)	163, 191, 203
acenaphthylene	0.83	40	152(100), 153(16), 151(17)	152, 153, 181
acenaphthene	0.86	40	154(100), 153(95), 152(53)	154, 155, 183
isophorone	0.87	40	82(100), 95(14), 138(18)	139, 167, 178
fluorene	0.91	40	166(100), 165(80), 167(14)	166, 167, 195
2,6-dinitrotoluene	0.93	40	165(100), 63(72), 121(23)	183, 211, 223
1,2-diphenylhydrazine	0.96	40*	77(100), 93(58), 105(28)	185, 213, 225
2,4-dinitrotoluene	0.98	40	165(100), 63(72), 121(23)	183, 211, 223
N-nitrosodiphenylamine	0.99	40*	169(100), 168(71), 167(50)	169, 170, 198
hexachlorobenzene	1.00	40	284(100), 142(30), 249(24)	284, 286, 288
4-bromophenyl phenyl ether	1.01	40	248(100), 250(99), 141(45)	249, 251, 277
phenanthrene	1.09	40	178(100), 179(16), 176(15)	178, 179, 207
anthracene	1.09	40	178(100), 179(16), 176(15)	178, 179, 207
dimethylphthalate	1.10	40	163(100), 164(10), 194(11)	151, 163, 164
diethylphthalate	1.15	40	149(100), 178(25), 150(10)	177, 223, 251
fluoranthene	1.23	40	202(100), 101(23), 100(14)	203, 231, 243
pyrene	1.30	40	202(100), 101(26), 100(17)	203, 231, 243
di-n-butylphthalate	1.31	40	149(100), 150(27), 104(10)	149, 205, 279
benzidine	1.38	40*	184(100), 92(24), 185(13)	185, 213, 225
butyl benzylphthalate	1.46	40	149(100), 91)50)	149, 299, 327

Table IV. Base-neutral Extractables (Cont'd.)

Compound Name	RRT[1] (hexachloro-benzene)	Limit of Detection (ng)	Characteristic EI ions (Rel. Int.)	CI ions (Methane)
chrysene	1.46	40	228(100), 229(19), 226(23)	228, 229, 257
bis(2-ethylhexyl)phthalate	1.50	40	149(100), 167(31), 279(26)	149
benzo(a)anthracene	1.54	40	228(100), 229(19), 226(19)	228, 229, 257
benzo(b)fluoranthene	1.66	40	252(100), 253(23), 125(15)	252, 253, 281
benzo(k)fluoranthene	1.66	40	252(100), 253(23), 125(16)	252, 253, 281
benzo(a)pyrene	1.73	40	252(100), 253(23), 125(21)	252, 253, 281
indeno(1,2,3-cd)pyrene	2.07	100	276(100), 138(28), 277(27)	276, 277, 305
dibenzo(a,h)anthracene	2.12	100	278(100), 139(24), 279(24)	278, 279, 307
benzo(g h i)perylene	2.18	100	276(100), 138(37), 277(25)	276, 277, 305
N-nitrosodimethylamine			42(100), 74(88), 44(21)	
N-nitrosodi-n-propylamine			130(22), 42(64), 101(12)	
4-chloro-phenyl phenyl ether			204(100), 206(34), 141(29)	
endrin aldehyde				
3,3'-dichlorobenzidine			252(100), 254(66), 126(16)	
2,3,7,8-tetrachlorodibenzo-p-dioxin			322(100), 320(90), 59(95)	
bis(chloromethyl)ether			45(100), 49(14), 51(5)	
deuterated anthracene (d10)	1.09	40	188(100), 94(19), 80(18)	189, 217

[1] 1% SP-2250 on 100/120 mesh Supelcoport in a 6' x 2 mm id glass column; He @ 30 ml/min; Program: 50° for 4 min, then 8°/min to 260° and hold for 15 min.

* Conditioning of column with base is required.

Table V. Acid Extractables

Compound Name	RRT[1] (2-nitrophenol)	Limit of Detection (ng)	Characteristic EI ions (Rel. Int.)	CI ions (Methane)
2-chlorophenol	0.63	100	128(100), 64(54), 130(31)	129, 131, 157
phenol	0.66	100	94(100), 65(17), 66(19)	95, 123, 135
2,4-dichlorophenol	0.96	100	162(100), 164(58), 98(61)	163, 165, 167
2-nitrophenol	1.00	100	139(100), 65(35), 109(8)	140, 168, 122
p-chloro-m-cresol	1.05	100	142(100), 107(80), 144(32)	143, 171, 183
2,4,6-trichlorophenol	1.14	100	196(100), 198(92), 200(26)	197, 199, 201
2,4-dimethylphenol	1.32	100	122(100), 107(90), 121(55)	123, 151, 163
2,4-dinitrophenol	1.34	2 µg	184(100), 63(59), 154(53)	185, 213, 225
4,6-dinitro-o-cresol	1.42	2 µg	198(100), 182(35), 77(28)	199, 227, 239
4-nitrophenol	1.43	100	65(100), 139(45), 109(72)	140, 168, 122
pentachlorophenol	1.64	100	266(100), 264(62), 268(63)	267, 265, 269
deuterated anthracene (d10)	1.68	40	188(100), 94(19), 80(18)	189, 217

[1] Column: 6' glass, 2 mm i.d.
Tenax GC - 60/80 mesh
180° - 300° @ 8°/min.
He @ 30 ml/min

Table VI. ELUTION ORDER OF MOST OF THE SEMIVOLATILE PRIORITY POLLUTANTS ON 1% SP2250[a]

Compound	RRT[b,c]
1,3-dichlorobenzene	0.35[d]
2-chlorophenol	0.35[e]
1,4-dichlorobenzene	0.36[d]
hexachloroethane	0.38
1,2-dichlorobenzene	0.39
bis(2-chloroisopropyl)ether	0.47
β-endosulfan	0.51
2,4-dimethyl phenol	0.52[e]
2-nitrophenol	0.53[e]
2,4-dichlorophenol	0.53[e]
hexachlorobutadiene	0.55
1,2,4-trichlorobenzene	0.55
naphthalene	0.57
bis(2-chloroethyl)ether	0.61
hexachlorocyclopentadiene	0.64
nitrobenzene	0.64
phenol	0.67
bis(2-chloroethoxy)methane	0.68
2,4,6-trichlorophenol	0.71[e]
p-chloro-m-cresol	0.73[f]
2-chloronaphthalene	0.76
acenaphthylene	0.83
acenaphthene	0.86
isophorone	0.87
fluorene	0.91

Table VI. ELUTION ORDER OF MOST OF THE SEMIVOLATILE PRIORITY POLLUTANTS ON 1% SP2250[a] (Continued)

Compound	RRT[b,c]
2,6-dinitrotoluene	0.93
1,2-diphenylhydrazine	0.96
2,4-dinitrotoluene	0.98
N-nitrosodiphenylamine	0.99
hexachlorobenzene	1.00
4-bromophenyl phenyl ether	1.01
α-BHC	1.02
γ-BHC	1.09[f]
phenanthrene	1.09[f]
anthracene	1.09
dimethyl phthalate	1.10
pentachlorophenol	1.11[f]
β-BHC	1.12
aldrin	1.14
diethyl phthalate	1.15
heptachlor	1.15
heptachlor epoxide	1.23
fluoranthene	1.23
α-endosulfan	1.24
dieldrin	1.28
4,4'-DDE	1.30
pyrene	1.30
di-n-butyl phthalate	1.31
4,4'-DDD (p,p'-TDE)	1.33
4,4'--DDT	1.38[d]
endosulfan sulfate	1.41[f]
endrin	1.41
benzidine	1.38
butyl benzyl phthalate	1.46
chrysene	1.46

Table VI. ELUTION ORDER OF MOST OF THE SEMIVOLATILE PRIORITY POLLUTANTS ON 1% SP2250[a] (Continued)

Compound	RRT[b,c]
bis(2-ethylhexyl)phthalate	1.50
benzo(a)anthracene	1.54
benzo(b)fluoranthene	1.66
benzo(k)fluoranthene	1.66
benzo(a)pyrene	1.73
indeno(1,2,3-cd)pyrene	2.07
dibenzo(a,h)anthracene	2.12[d]
benzo(ghi)perylene	2.12[f]

[a] 1% SP-2250 on 100/120 mesh Supelcoport in a 6' x 2mm id glass column; He @ 30ml/min; Program: 50° for 4 min, then 8°/min to 260° and hold for 15 min.

[b] Relative to hexachlorobenzene at 19.4 min.

[c] 40ng gives 5-90% response on FID unless otherwise noted.

[d] 200ng required to obtain 5-90% response on FID.

[e] 2 µg required.

[f] 40 µg required.

Table VI

(continued)

Standards not available: as of 2/8/77

N-nitrosodi-n-propylamine
4-chlorophenyl phenyl ether
TCDD
endrin aldehyde
N-nitrosodimethylamine
3,3'-dichlorobenzidine
bis(chloromethyl)ether (unstable in water)

Standards that would not chromatograph:

4,6-dinitro-o-cresol
4-nitrophenol
2,4-dinitrophenol

Standards yielding a range of peaks:

	RRT[b]
PCB-1242	0.93-1.24
PCB-1254	1.18-1.41
toxaphene	1.22-1.47
chlordane	1.14-1.37

Table VII. Order of Elution for OV-17 SCOT Column[1]

Compound	Spectrum Number[2]
1,3-dichlorobenzene	134
1,4-dichlorobenzene	137
2-chlorophenol	141
1,2-dichlorobenzene	153
bis(2-chloroethyl)ether	163
phenol	165
bis(2-chloroisopropyl)ether	173
hexachloroethane	178
nitrobenzene	194
2-nitrophenol	219
1,2,4-trichlorobenzene	234
2,4-dimethylphenol	240
naphthalene	240
2,4-dichlorophenol	244
hexachlorobutadiene	262
isophorone	272
p-chloro-m-cresol	317
hexachlorocyclopentadiene	325
2,4,6-trichlorophenol	332
chloronaphthalene	339
2,4-dinitrotoluene	372
acenaphthylene	374
acenaphthene	390
dimethylphthalate	397
fluorene	434
diethylphthalate	447
N-nitrosodiphenylamine	447
2,6-dinitrotoluene	454
α-BHC	476
4-bromophenyl phenyl ether	478
γ-BHC	487
hexachlorobenzene	490
β-BHC	506
phenanthrene	518
anthracene	518
di-n-butylphthalate	583
aldrin	592
fluoranthene	617
pyrene	634
DDE	659
DDD	664
endrin	688
dieldrin	688
DDT	713
butyl benzyl phthalate	713
benzo(a)anthracene	748
chrysene	748

Table VII. Continued

Compound	Spectrum Number[2]
bis(2-ethylhexyl)phthalate	804
benzo(a)pyrene	906
benzo(b)fluoranthene	970
benzo(k)fluoranthene	970

[1] 33 meter glass OV-17 SCOT column,
Program: 60° - 260° @ 6°/minute

[2] Number of 2.5 second scans up to point of elution.

Metals

1. Sample Preparation

With the exception of mercury, the metals to be determined may be divided into two groups as follow:

a) those metals which are to be first analyzed by flame atomic absorption (AA), and, if not detected, then analyzed by flameless AA--Be, Cd, Cr, Cu, Ni, Pb and Zn,

b) those metals which are to be analyzed by flameless AA only--Ag, As, Sb, Se, and Tl.

For flame AA analysis the sample should be prepared using the procedure as given in "Methods for Chemical Analyses of Water and Wastes (1974)", 4.1.4, page 83 (Reference 7).

With the exception of antimony and beryllium, samples to be analyzed by flameless AA should be prepared as an industrial effluent as described in "Atomic Absorption Newsletter," 14, page 111 (1975) (Reference 8). Note: Nickel nitrate should be added only to those aliquots on which the analysis of selenium and arsenic are to be accomplished. The sample preparation procedure for antimony and beryllium analysis by flameless AA is the same procedure used for flame AA.

The sample preparation procedure to be used for mercury analysis is that given in "Methods for Chemical Analysis of Water and Wastes (1974)", 8.1, page 124 (Reference 7).

2. Apparatus

All samples are to be analyzed using an atomic absorption spectrophotometer equipped with simultaneous background capability. For arsenic, cadmium, antimony, selenium, thallium, and zinc, either electrodeless discharge lamps or high intensity hollow cathode lamps may be utilized. A heated graphite atomizer is to be used for all flameless AA work. A strip chart recorder must be used as part of the readout system to detect and avoid the inclusion of extraneous data.

3. Procedure

a) Flame AA - The procedures to be used are those described in "Methods for Chemical Analysis of Water and Wastes (1974)"(Reference 7) as referenced in Table I below. Instructions as to when flameless AA is to be used are also included. For those defined in the recommended procedures, the instrument manufacturers recommendations are to be followed. Background correction is to be used on all analyses.

Table VIII

Element	Methods for Chemical Analysis of Water and Wastes, 1974*	Comments
Be	p. 99	Analyze by flameless AA if conc. <20 µg/l
Cd	p. 101	Analyze by flameless AA if conc. <20 µg/l
Cr	p. 105	Use nitrous oxide-acetylene flame for all analyses--analyze by flameless AA if conc. <200 µg/l
Cu	p. 108	Analyze by flameless AA if conc. <50 µg/l
Ni	p. 141	Analyze by flameless AA if conc. <100 µg/l
Pb	p. 112	Analyze by flameless AA if conc. <300 µg/l
Zn	p. 155	Analyze by flameless AA if conc. <20 µg/l

*In those instances where more vigorous digestion for sample preparation is desired (or necessary) the procedure on page 82 (4.1.3) should be followed.

b) Standard solutions to be used for the flameless work should also be prepared as described in "Methods for Chemical Analysis of Water and Wastes (1974)" (Reference 7). The working standards should be diluted to contain the same acid concentration as the prepared samples. The instrumental settings and conditions recommended by the manufacturers are to be considered the procedural guidelines. In addition, the following requirements should also be incorporated into the procedures:

1) Argon should be used as the purge gas in all analyses.

2) Background correction and method of standard addition must be used on all analyses.

3) A blank maximum temperature atomization, without gas interrupt, should be accomplished before each analytical determination.

4) The graphite tube or cuvette should be replaced as suggested by the instrument manufacturer or when contamination or lack of precision indicates that replacement is necessary.

5) All disposable pipet tips should be cleaned before use by soaking overnight in 5% redistilled nitric acid, rinsed with tap and deionized water, and dried.

6) The accuracy of the temperature indicator on the heated graphite atomizer should be verified before beginning any analytical work. This should be done by plotting charring temperature for a standard solution of a compound where the volatilization temperature is known. The compound used should have a volatilization temperature between 800 and 1200°C.

7) To insure that there is no loss from the acid matrix prior to atomization, the optimum charring temperature for each metal should be established in the same manner (i.e., by plotting charring temperature versus atomization signal of standard solution of each metal).

For the determination of selenium the procedure given for industrial effluents ("Atomic Absorption Newsletter," Vol. 14, page 109 [1975]) (Reference 8) should be followed. Arsenic should be determined in the same manner (using the nickel nitrate matrix) with an optimum charring temperature of approximately 1300°C.

The analysis of zinc by flameless AA is difficult because of environmental contamination. The analyst must take precaution to provide a clean work area to minimize this problem.

c) Mercury analyses - The cold vapor technique as described in "Methods for Chemical Analysis of Water and Wastes, (1974)", page 118 (Reference 7) is to be followed.

4. Quality Assurance

a) To verify that the instrument is operating correctly within the expected performance limits, an appropriate standard should be included between every ten samples.

b) Spiked aliquots shall be analyzed with a frequency of 15% of the sample load for each metal determined by flame AA. If the recovery is not within ±10% of the expected value the sample should be analyzed by method of standard addition. (The spike should be added to the aliquot prior to sample preparation.) The amount added should increase the absorbance by not less than 0.01 units where the absorbance in the unspiked aliquot was less than 0.1, and not more than 0.1 when the absorbance in the unspiked aliquot was 0.1 or greater.

c) For mercury, the spike added should be an amount equal to five times the detection level.

d) Reagent blanks shall be run for each metal being determined with the sample values being corrected accordingly.

e) When using the method of standard addition, a linear curve over the entire range of addition is necessary for the results to be considered valid.

5. Data Reporting

Report all metal concentrations as follows: Less than 10 µg/l, nearest µg; 10 µg/l and above, two significant figures.

Cyanides

1. Sample Preparation

All samples are to be distilled prior to determination for total cyanides. The distillation procedure given on page 43 of "Methods for Chemical Analysis of Water and Wastes, (1974)" (Reference 7) is to be followed.

2. Sample Procedure

The procedure for total cyanides as given on pages 43-48 of "Methods for Chemical Analysis of Water and Wastes, (1974)" (Reference 7) is to be followed.

3. Quality Assurance

a) Initially, demonstrate quantitative recovery with each distillation-digestion apparatus by comparing distilled standards to non-distilled standards. Each day, distill at least one standard to confirm distillation efficiency and purity of reagents.

b) At least 15% of the cyanide analysis will consist of duplicate and spiked samples. Quality control limits are to be established and confirmed as described in Chapter 6 of the "Analytical Quality Control Handbook" (Reference 9).

4. Reporting of Data

Report cyanide concentrations as follows: Less than 1.0 mg/l, nearest 0.01 mg; 1.0 mg/l and above, two significant figures.

Phenols

1. Sample Preparation

Distill all samples prior to determination of phenols. Use the procedure in "Standard Methods for the Examination of Water and Wastewater," 14th edition, 1975, p. 576 (Reference 10).

2. Procedure

Use method 510 for phenols in Appendix X, pages 577-580 and 580-581. Use method 510B for samples that contain less than 1 mg/l of phenol. Use method 510C for samples that contain more than 1 mg/l of phenol.

3. Quality Assurance

Demonstrate quantitative recovery with each distillation apparatus by comparing distilled standards to non-distilled standards. Each day distill, at least, one standard to confirm the distillation efficiency and purity of reagents.

Run duplicate and dosed sample analyses on at least 15% of the samples analyzed for phenol. Establish and confirm quality control limits as described in Reference 9.

4. Reporting of Data

Report phenol concentrations as follows:

Method 510B to the nearest µg/l.

Method 510C - when less than 1.0 µg/l to the nearest 0.01 mg; 1.0 mg/l and above to two significent figures.

Report all quality control data when reporting results of sample analysis.

REFERENCES

1. Determining Volatile Organics at Microgram-per-Liter Levels by Gas Chromatography. T. A. Bellar and J. J. Lichtenberg, Jour. AWWA, p. 739-744, Dec. 1974.

2. Reference Compound to Calibrate Ion Abundance Measurements in Gas Chromatography--Mass Spectrometry Systems. J. W. Eichelberger, L. E. Harris and W. L. Budde, Anal. Chem. 47, 995-1000 (1975).

3. ASTM Annual Standards - Water, part 31, Method D2908 "Standard Recommended Practice for Measuring Water by Aqueous-Injection Gas Chromatography."

4. ASTM Annual Standards - Water, part 31, Method D3371 "Tentative Method of Test for Nitriles in Aqueous Solution by Gas Liquid Chromatograph."

5. Harris, L. E., Budde, W. L. and Eichelberger, J. W., Anal. Chem., 46, 1912 (1974). "Direct Analysis of Water Samples for Organic Pollutants with Gas Chromatography-Mass Spectrometry."

6. Federal Register, Volume 38, number 125, part II, Appendix II, p. 17319, Friday, June 29, 1975, "Determination of Organochlorine Pesticides in Industrial Effluents,"

7. Methods for Chemical Analysis of Water and Wastes (1974). U.S. Environmental Protection Agency, Technology Transfer.

8. Determining Selenium in Water, Wastewater, Sediment and Sludge by Flameless Atomic Absorption Spectroscopy. T. D. Martin and J. F. Kopp, Atomic Absorption Newsletter 14, 109-116 (1975).

9. Handbook for Analytical Quality Control in Water and Wastewater Laboratories (1972). U.S. Environmental Protection Agency, Technology Transfer.

10. "Standard Methods for the Examination of Water and Wastewater," 14th edition, 1975.

APPENDIX I

General Information

Emulsions

Limited work with several categories of industrial effluents covered by this study (tanneries, petroleum, soap and detergent, steam electric, pesticide) show that emulsions of widely differing frustration factors are often encountered in the extraction procedure. Samples that emulsify at basic pH usually also emulsify at acid pH. There are two equally acceptable alternatives available for the purposes of this protocol: break the emulsion or start over with fresh sample and use a continuous extractor, to prevent the formation of emulsions.

By the 85% solvent recovery criteria, no way was found to break the emulsion formed on extraction of untreated tannery wastes. A soap and detergent sample was also very difficult. The use of a continuous heavier-than-water liquid extractor allowed the extraction to take place with no difficulties and very little labor. However, two days time is required. Comparison of samples from four industries--petroleum, tannery, pesticide, and soap and detergent--by both shake-out and continuous extraction using wastes spiked with priority pollutants indicate that the two techniques are comparable. For some individual cases one technique is better than the other but no clear pattern emerges. Therefore, if desired, a continuous extraction technique may be used in place of separatory funnel extraction for all samples as well as those for which it is absolutely necessary because of intractable emulsions.

APPENDIX I

(continued)

There is a justifiable concern that the extraction efficiency for these compounds may differ widely depending on the nature of the effluents. This is true but no better approach is apparent. For example, recoveries of most of the base-neutrals were judged to be about 75% from the tannery and petroleum samples but less than 25% from soap and detergent.

Acid (Phenol) Analysis

Although the 11 phenols of interest here do chromatograph on the Tenax column cited, the chromatography is poor, particularly for the nitrophenols. Two other columns have shown good response for the acid extractables. SP2250 can be used for this purpose. Phenol responses on SP2250 are shown in Table IV. It should be noted, however, that 4-nitrophenol, 2,4-dinitrophenol, 4,6-dinitro-o-cresol, and pentachlorophenol failed to give MS response at the 100 ng level using this column.

SP1000 (4% load) has also been evaluated for use with the acid fraction. All but 2,4-dinitrophenol and 4,6-dinitro-o-cresol elute from this column. Pentachlorophenol and 4-nitrophenol are eluted from SP1000, but they produce broad peaks which are difficult to quantify.

Appendix II

Possible Sources for Some Priority Pollutant Standards

Compound	Source of Standard[2]
acenaphthene	AN p. 118
acrolein	AL p. 18
acrylonitrile	AL p. 19
aldrin	HERL #80
dieldrin	HERL #2380
benzene	B p. 154
benzidine[1]	RFR
carbon tetrachloride (tetrachloromethane)	B p. 88
chlordane (technical mixture & metabolites)	HERL #1200
Chlorinated benzenes (other than dichlorobenzenes)	
chlorobenzene	AL p. 165
1,2,4-trichlorobenzene	AL p. 710
hexachlorobenzene	AL p. 416
Chlorinated ethanes (including 1,2-dichloroethane, 1,1,1-trichloroethane and hexachloroethane)	
1,2-dichloroethane	AL p. 261
1,1,1-trichloroethane	B p. 309
hexachloroethane	AL p. 416
1,1-dichloroethane	PB p. 142
1,1,2-trichloroethane	PB p. 388
1,1,2,2-tetrachloroethane	PB p. 372
chloroethane	EA p. 53
Chloroalkyl ethers (chloromethyl, chloroethyl and mixed ethers)	
bis(chloromethyl) ether[1]	RFR
bis(2-chloroethyl) ether	AL p. 173
2-chloroethyl vinyl ether	AL p. 174
Chlorinated naphthalene	
2-chloronaphthalene	ICN p. 50

Appendix II

Possible Sources for Some Priority Pollutant Standards
(Continued)

Compound	Source of Standard[2]
Chlorinated phenols (other than those listed elsewhere; includes trichlorophenols and chlorinated cresols)	
2,4,6-trichlorophenol	AL p. 712
p-chloro-m-cresol	TCI p. 102
chloroform (trichloromethane)	B p. 92
2-chlorophenol	AL p. 187
DDT and metabolites	
4,4'-DDT	HERL #1920
4,4'-DDE	HERL #1860
4,4'-DDD (p,p'-TDE)	HERL #1780
Dichlorobenzenes (1,2-;1,3-; and 1,4-dichlorobenzenes)	
1,2-dichlorobenzene	AL p. 258
1,3-dichlorobenzene	AL p. 258
1,4-dichlorobenzene	AL p. 258
Dichlorobenzidine	
3,3'-dichlorobenzidine[1]	CPL p. 81
Dichloroethylenes (1,1-dichloroethylene and 1,2-dichloroethylene)	
1,1-dichloroethylene	AL p. 746
1,2-trans-dichloroethylene	AL p. 262
2,4-dichlorophenol	AL p. 265
Dichloropropane and dichloropropene	
1,2-dichloropropane	AL p. 267
1,3-dichloropropylene (1,3-dichloropropene)	AL p. 267
2,4-dimethylphenol	AL p. 323
Dinitrotoluene	
2,4-dinitrotoluene	PB p. 180
2,6-dinitrotoluene	PB p. 180
1,2-diphenylhydrazine	AL p. 338

Appendix II

Possible Sources for Some Priority Pollutant Standards

(Continued)

Compound	Source of Standard[2]
Endosulfan and metabolites	
α-endosulfan	HERL #3220
β-endosulfan	HERL #3200
endosulfan sulfate	NI p. 45
Endrin and metabolites	
endrin	HERL #3260
endrin aldehyde	NI p. 147
ethylbenzene	B p. 161
fluoranthene	AN p. 118
Haloethers (other than those listed elsewhere)	
4-chlorophenyl phenyl ether (p-chlorodiphenyl ether)	RFR p. 6*
4-bromophenyl phenyl ether	ICN p. 37
bis(2-chloroisopropyl) ether	PB
bis(2-chloroethoxy) methane	PB p. 62
Halomethanes (other than those listed elsewhere)	
methylene chloride (dichloromethane)	PB p. 276
methyl chloride (chloromethane)	PB p. 277
methyl bormide (bromomethane)	PB p. 276
bromoform (tribromomethane)	PB p. 73
dichlorobromomethane	CO p. 16
trichlorofluoromethane	PB p. 358
dichlorodifluoromethane	PB p. 142
chlorodibromomethane	CO p. 27
Heptachlor and metabolites	
heptachlor	HERL #3860
heptachlor epoxide	HERL #3880
hexachlorobutadiene	AL p. 416
Hexachlorobyclohexane (all isomers)	
α-BHC	HERL #620
β-BHC	HERL #640
γ-BHC (lindane)	HERL #680
δ-BHC	HERL #660

Appendix II

Possible Sources for Some Priority Pollutant Standards
(Continued)

Compound	Source of Standard[2]
hexachlorocyclopentadiene	AL p. 416
isophorone	AL p. 464
naphthalene	AN p. 118
nitrobenzene	AL p. 557
Nitrophenols (including 2,4-dinitrophenol and dinitrocresol)	
2-nitrophenol	AL p. 564
4-nitrophenol	AL p. 564
2,4-dinitrophenol	AL p. 332
4,6-dinitro-o-cresol	TCI p. 188
Nitrosamines	
N-nitrosodimethylamine[1]	NI p. 173
N-nitrosodi-n-propylamine	PB p. 310
N-nitrosodiphenylamine	EA p. 159
pentachlorophenol	AL p. 587
phenol	AL p. 595
Phthalate esters	
bis(2-ethylhexyl) phthalate	CS p. 8
butyl benzyl phthalate	CS p. 8
di-n-butyl phthalate	CS p. 8
diethyl phthalate	CS p. 8
dimethyl phthalate	CS p. 8
Polychlorinated biphenyls (PCB's)	
PCB-1242 (Arochlor 1242)	HERL #5703
PCB-1254 (Arochlor 1254)	HERL #5705
Polynuclear aromatic hydrocarbons (including benzanthracenes, benzopyrenes, benzofluoranthene, chrysenes, dibenzanthracenes, and indenopyrenes)	
1,2-benzanthracene	AN p. 118
benzo[a]pyrene (3,4-benzopyrene)	AN p. 118
3,4-benzofluoranthene	NI
11,12-benzofluoranthene	NI
chrysene	AN p. 118

Appendix II

Possible Sources for Some Priority Pollutant Standards

(Continued)

Compound	Source of Standard[2]
acenaphthylene	AN p. 1
anthracene	AN p. 118
1,12-benzoperylene	AN p. 118
fluorene	AN p. 118
phenanthrene	AN p. 118
1,2:5,6-dibenzanthracene	AN p. 118
indeno (1,2,3-C,D)pyrene	AN p. 118
pyrene	AN p. 118
2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)	NI p. 174
tetrachloroethylene	AL p. 680
toluene	AL p. 701
toxaphene	HERL #6740
trichloroethylene	AL p. 711
vinyl chloride (chloroethylene)	PB p. 406
1-bromodecane (possible internal standard)	
1-bromododecane (possible internal standard)	

Footnotes:

[1] These compounds or any mixture containing 1% or more by weight of these compounds are defined as carcinogens in the Federal Register, Vol. 38, No. 144, pp. 20074-20076, 27 July 1973. Prescribed safety regulations for handling are in the Federal Register, Vol. 39, No. 20, pp. 3756-3797, 29 January 1974.

[2] Only one source is listed even though several may be available. These sources are not to be interpreted as being endorsed by the EPA; they serve to show at least one vendor where each standard can be obtained. When several sources were available and compound purity was listed, the source having the highest purity material was selected.

* These compounds have been ordered but have not been received at Athens ERL as yet.

Sources of Standards and Abbreviations

AL	Aldrich Chemical Co., Milwaukee, Wisc.; Catalog 1977-1978.
AN	Analabs, Inc., North Haven, Conn.; Catalog 18 (June 1976).
B	J. T. Baker Chemical Co., Phillipsburgh, N.J.; Catalog 750 (July 1975).
CS	Chem-Service, West Chester, Pa.; Bulletin CS-100-8 (1975).
CPL	Chemical Procurement Laboratories, College Point, N.Y.; 1975 catalog.
EA	Eastman Kodak Co., Rochester, N.Y.; Catalog 48 (1976).
ICN	K&K Rare & Fine Chemicals, Plainview, N.Y.; Catalog No. 10 (1975).
NI	Nanogens International, P.O. Box 487, Freedom, CA 95019 "Nanogen Index" (1975).
PB	Pfaltz & Bauer Chemical Co., STamford, Conn.; Catalog 1976.
RFR	RFR Corp., Hope, R.I.; "Chemical Standards for Air-Water-Industry-Foods" (1975).
HERL	"Analytical Reference Standards and Supplemental Data for Pesticides and Other Selected Organic Compounds", EPA-660/9-76-012 (May 1976), Health Effects Research Laboratory, Environmental Toxicology Division, Research Triangle Park, NC. A sample order blank for standards and the above publication are attached.
CO	Columbia Organics Catalog A-7, Columbia, S.C. (1975).
TCI	Tridom Chemical Inc., Hauttauge, N.Y., Catalog No. 1 (1976).

*Those labs which are under contract to perform GC-MS analysis for EPA, may obtain a set of standards from Mr. William A. Telliard, Chief, Energy and Mining Branch, Effluent Guidelines Division, (WH 552) 401 M Street, S.W. Washington, D.C. 20460 (202) 426-2726.

ENVIRONMENTAL TOXICOLOGY DIVISION
HEALTH EFFECTS RESEARCH LABORATORY
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina 27711

SUBJECT: Index of Pesticides Analytical Reference Standards - Update of Mailing List

DATE: June, 1976

FROM: Health Effects Research Laboratory, ETD, ACB, Research Triangle Park, NC, U.S.A. 27711 (MD-69) J. F. Thompson

TO: All Laboratory Facilities on our Mailing List

This copy of the 1976 revision of our pesticides reference standards index was mailed to the address appearing on our mailing list. As this list is several years old, we are sure that a number of addresses have changed and that some are probably no longer existent.

If you wish to remain on our mailing list to receive future updates of this publication, would you be good enough to complete the mail-back below, snip it off, and return it to us. Do not tear off the back cover to return to the address shown. If you have no use for this publication but know of some other individual within your organization who is concerned with pesticides analysis, would you convey this index, along with the mailback, to that person.

To: U. S. Environmental Protection Agency
Health Effects Research Laboratory
Environmental Toxicology Division
Research Triangle Park, NC, U.S.A. 27711 (MD-69)

Date: _____

☐ We wish to be retained on your mailing list to receive future updates of the Pesticides Standards Index. The address shown on the envelope is entirely correct and requires no changes.

☐ We have no interest in future updates of this publication. Please cancel us from your mailing list.

☐ We wish to be retained on your mailing list, but the address shown on the envelope should be changed to read (print or type)

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REQUEST FOR ANALYTICAL REFERENCE STANDARDS

Date

TO: Quality Assurance Section
Environmental Toxicology Division,
EPA, HERL, Research Triangle Park, NC 27711
MD-69

Date Request Recd	/ /
Shipment Date	/ /
Lab Code No.	
Order Filled by	
DO NOT WRITE IN THIS SPACE	

The following reference standards are required for our program:

Catalog Code No.	Compound (Catalog Name)	Catalog Code No.	Compound (Catalog Name)

If necessary, use back of sheet to complete list. Covering letter unnecessary if this form is completed in full.

Name and address of laboratory _____

_____

_____

_____

_____

Requestor's Name (Print or type)

IMPORTANT:

1. The amount of each standard is restricted to 100 mg because of the scarcity and expense of refining analytical grade materials.

2. Please return at once the acknowledgement card enclosed with each shipment. This provides the sole evidence of delivery of the shipment.

3. Do not request compounds not listed in the catalog. No others are stocked.

4. If a bottle appears to be empty, remove cap and examine interior of bottle and cap. Certain highly viscous materials tend to collect in cap.

APPENDIX III

COLLECTION OF SAMPLES FOR SCREENING ANALYSES

The initial characterization (screening) of the varied industrial discharges covered by this program will be made on an analysis of a composite effluent sample. Any scheme for collecting a composite sample is, in effect a method for mechanically integrating to obtain average characteristics of a discharge. During the screening phase the sample composite can be used to determine the average characteristics which would be representative of that discharge. Simple composite samples are those that are made up of a series of aliquots of constant volume collected at regular time intervals in a single container. Some situations may require flow or time proportional sampling, this determination will be made by the individual project officer after considering his specific industrial category.

The determination of compositing period 24, 48 or 72 hours will be made on a case by case basis. The duration of compositing will depend on the type of sample being collected, the type of facility being sampled and the time varying characteristics of the discharge. The rate of change of flow and other characteristics of the discharge and the accuracy required will also influence the determination of the compositing period. For example longer compositing periods would be warranted when less stable unit process operations are being sampled.

Collection of Samples

1. Collection of Composite Samples for Liquid-Liquid Extraction

Collect a representative composite sample. The maximum time interval between aliquot samples shall be no longer than 30 minutes. The minimum aliquot size shall be 100 ml. The sample must be collected with an automatic sampler using the equipment and methods outlined below. Minimum composite volume must be 2 1/2 gallons.

Automatic Sample Collection

Sampler - A peristaltic pump automatic sampler with timer and a single glass compositing jug is required. The 2 1/2 - 3 gallon compositing bottle must be glass and cleaned

as outlined below. New unused tubing must be used for the sampling line and for the pump for each individual outfall or sample location. Vacuum type automatic samplers may be used provided that the sample chambers are glass and that they are cleaned after every use as outlined for glass composite containers. Place the sampler or composite container in an insulated chest and ice. Maintain the sample at 4°C during the compositing procedure. At the completion of the compositing period seal the container with a teflon lined cap. Place the container in an insulated shipping container, ice, and seal, then ship to the analytical laboratory. Maintain at 4°C during transport and storage prior to analysis.

When sampling raw untreated industrial discharges which are generally high in suspended solids it is imperative that adequate sample flow rate be maintained throughout the sample train in order to effectively transport the solids. In horizontal runs, the velocity must exceed the scour velocity, while in vertical runs the settling or the fall velocity must be exceeded several times to assure adequate transport of solids in the flow. The equipment used in sampling raw discharges then must have a minimum intake velocity of 2 feet per second. In the sampling of treated effluents just about any commerically available automatic liquid sampler could be used.

When more than one laboratory is involved in the analysis of the various parameters, the sample should if at all possible not be divided in the field but rather at the contractors' laboratory. For purpose of this program the composite will be divided into four parts, one part for metals analysis, one for pesticides and PCB's, one for GC/MS compounds and one for the classic parameters.

Blend the composite sample to provide a homogeneous mixture including a representative suspension of any solids in the container. No specific method is required, hand stirring with clean glass or teflon rods, mechanical paddles or magnetic mixing with teflon coated stirring bars may be used. Metal mixing devices may not be used.

Metals - Withdraw a well blended aliquot of the composite sample. Using a glass funnel, rinse the sample container with a small portion of the sample, then transfer

250 - 500 mg/l of sample to the bottle. Do not add any preservative to the sample just seal and prepare for shipment. All samples must be carefully identified using labeles supplied by EGD. Indicate on the label whether the sample is a raw discharge or treated effluent as shown. If sample is to be run on the plasma unit only indicate so at base of tag. Ship samples to the Chicago Regional Laboratory at the addressed shown.

U.S. Environmental Protection Agency
Region V, Central Regional Laboratory
1819 W. Pershing Road
Chicago, Illinois 60609

Raw discharge or treated effluent

EPA-EGD № V002200

Location_____

Sampler_____

Sample Point_____

Type Sample_____Grab_____Composite

Date_____to_____

Time_____to_____

Preservatives_____

Plasma only

Field Blank Procedure for Automatic Samplers

Blank Water - Blank water must be as free from organic interferences as possible. The analytical laboratory should supply this water in bulk glass containers (minimum of five liters) for field use. The supplying laboratory shall analyze the blank water to determine the organic background that may be present.

Procedure - All parts of the sampling system must be scrubbed with hot detergent water and thoroughly rinsed with tap water and blank water prior to use. Further rinsing with methylene chloride is required when parts permit, i.e., are not susceptible to dissolution by the solvent. (Note: Tygon plastic tubing is a source of phthalate ester contamination. Where its use is required, i.e., in the peristaltic pump, the length must be kept as short as possible. Teflon is acceptable and may be used in other parts of the sampling system as in intake lines. In the field, pump two liters of blank water through the sampling line and pump tubing and discard. Then pump three liters of blank water through the system and collect as a blank in a 1-gallon sample bottle that has been prepared as described below. Seal the bottle with a Teflon lined cap. Immediately ice the blank (4° C) and maintain at (4°C) during the transport and storage prior to analysis.

Composite Container - Prepare narrow-mouth glass sample bottles for use by washing with hot detergent water and thoroughly rinsing with tap water and blank water. Heat the bottles at 400°C in a muffle-furnace or dry heat sterilizer for 30 minutes or alternatively, rinse with methylene chloride and air dry at room temperature protected from atomspheric or other sources of contamination. Caps for the bottles must be lined with Teflon which has been solvent rinsed as above.

2. Collection of Grab Samples

Collect grab samples (minimum of one per day) for the analysis of phenol, cyanide, and volatile organics (purgable). Collect samples from the raw process discharge, the treated effluent, and the treated effluent after chlorination, when chlorination is practiced. It is recommended that the samples be collected from mid-channel at mid-depth. Samples should be collected at a turbulent, well mixed section of the channel.

Cyanide (Total)

Container - Use new one-liter plastic bottles that will not contaminate the sample. Wash the bottles and caps with hot water and thoroughly rinse with tap water and blank water.

Collect a 1-liter sample.

Pretreatment and Preservation - Oxidizing agents such as chlorine decompose many cyanides. Therefore, at time of collection, samples must be treated to eliminate such agents. Test a drop of the sample at the time of collection with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascrobic acid, a few crystals at a time, until a drop of the sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume. Then add 2 ml of 10 N sodium hydroxide per liter of sample (pH $\geq$ 12).

Seal the sample bottle and place in an insulated chest and ice (4°C). Seal the chest and ship to the analytical laboratory. Maintain at 4°C during transport and storage keep out of direct light prior to analysis.

Phenols

Container - Use new one-liter glass bottles. Wash the bottle and Teflon cap liner with hot water and thoroughly rinse with tap water and blank water.

Collect a 1-liter sample.

Preservation - At the time of collection, acidify the sample by addition of phospheric acid or sulfuric to pH 4. Note volume of acid added on sample tag. Seal bottle, place in insulated chest and ice (4°C). Seal chest and ship to analytical laboratory. Maintain at 4°C during transport and storage. Keep out of direct light prior to analysis.

Organics (Purge and Trap Method)

Containers - Use 45 to 125 ml screw cap glass vials with Teflon faced silcone septa:

Vials[a]- Pierce #13074 or equivalent

Septa[a]- Pierce #12722 or equivalent

Wash the bottles, septa, and caps with hot water and thoroughly rinse with tap water and blank water. Heat the bottles and septa at 105°C for one hour, cool to room temperature in an enclosed contaminant free area. When cool, seal bottles with septa (Teflon side down) and screw cap. Maintain the bottles in this condition until just prior to filling with blank water or sample.

[a] Available from Pierce, Inc. Box 117, Rockford, IL 61105.

Collect duplicates 45-125 ml samples each time samples are collected. Two blank water samples, sealed in 45 ml vials, are to accompany the sample bottles during shipment to and from the sampling site. If preservation for residual chlorine is to be used, collect four samples during each sampling period. Two should be preserved and two not preserved. Two preserved and two non-preserved blanks are to be provided.

Filling and Sealing Bottles - Slowly fill each container to overflowing. Carefully set the container on a level surface. Place the septum (Teflon side down) on the convex sample meniscus. Seal the sample with the screw cap. To insure that the sample has been properly sealed, invert the sample and lightly tap the lid on a solid surface. The absence of entrapped air bubbles indicates a proper seal. If air bubbles are present, open the bottle, add additional sample, and reseal. The sample must remain hermetically sealed until it is analyzed.

Preservation - Preservative (sodium thiosulfate or sodium bisulfite) is used to stabilize samples containing residual chlorine. The production of chloroform and other haloforms continues in such samples if they are not stabilized. Waste streams that have been treated with chlorine should be tested on

site to determine whether or not preservative is needed. If preservatation is required, collect both preserved and non-preserved samples. Wrap the samples with water proof packing material, place in an insulated chest and ice at 4°C. Maintain at 4°C during transport and storage prior to analysis.

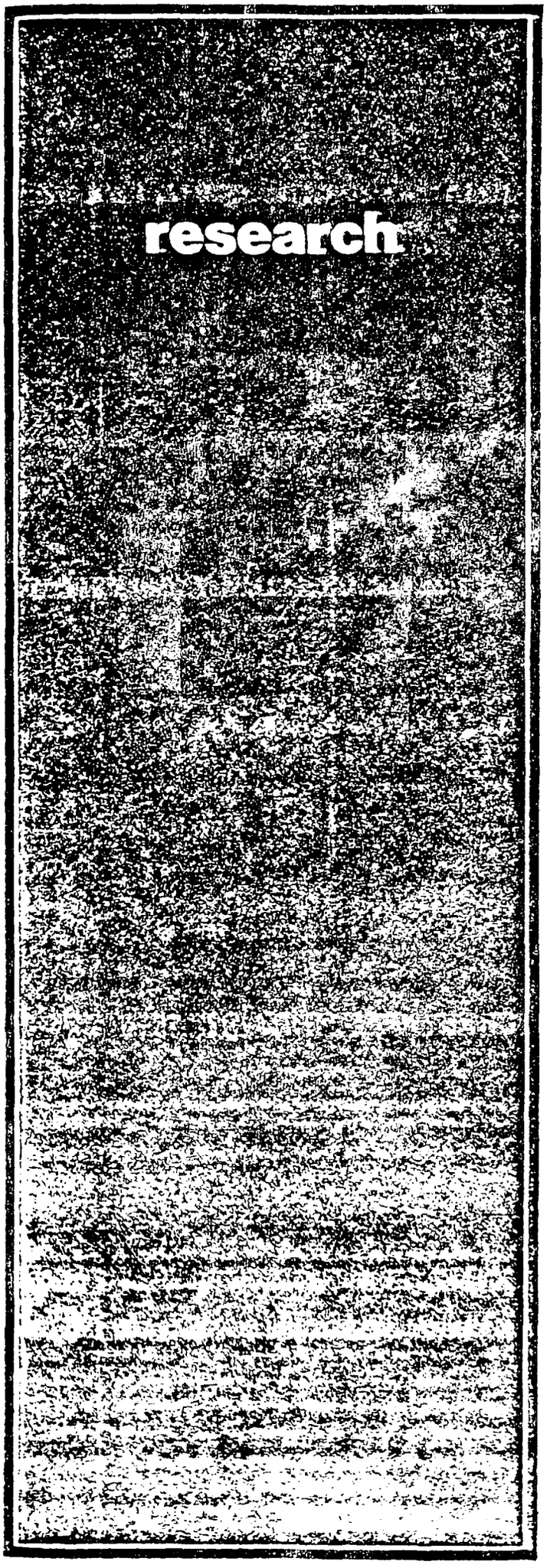
3. Identification of Samples

All samples and blanks must be carefully identified using water proof labels and water proof ink. Include the following information on the label: sample number, date and hour of sampling, complete information as to source and sampling point, preservative added, if any, and name of person collecting the sample (include address and/or phone number).

APPENDIX IV

REFERENCE NO. 1

DETERMINING VOLATILE ORGANICS AT MICROGRAM-PER LITER LEVELS



Determining Volatile Organics at Microgram-per-Litre Levels by Gas Chromatography

T. A. Bellar and J. J. Lichtenberg

A Metricized Article

A contribution submitted to the JOURNAL on Nov. 7, 1974, by T. A. Bellar and J. J. Lichtenberg, res. scientists, Methods Dev. and Qual. Assurance Res. Lab., EPA, Natl. Envir. Res. Ctr., Cincinnati, Ohio.

Presented here is a method for quantitative recovery of volatile organic compounds followed by a description of apparatus and procedures employed to detect 0.5 μg/l of the substances.

Recent legislation[1, 2] requires analytical methods for the determination of hydrocarbon and chlorinated organic solvents in wastewater. In some cases a minimum detectable limit of 1 μg/l (10^{-3}ppm) is required for specific compounds. It is the responsibility of the EPA's Methods Dev. and Qual. Assurance Res. Lab. to evaluate existing methods, and when necessary, to develop new methods to meet such needs.

Determination of these substances at the 1-μg/l (10^{-3}ppm) level has been difficult. Commonly used techniques such as direct aqueous-injection gas chromatography, liquid–liquid extraction, and head-gas analysis have proved inadequate. Direct aqueous-injection gas chromatography[3, 4] although generally useful for analysis of industrial effluents, provides an approximate limit of detection of only 1 000 μg/l (1 ppm).

Liquid–liquid extraction methods using low[5] or high[6] boiling organic solvents followed by gas-chromatographic analyses have been investigated. These methods have provided erratic or low extraction efficiencies for volatile compounds. In addition large solvent responses and solvent impurities can cause serious chromatographic interferences. Distillation techniques[7] have been employed in which a small quantity of sam ple distillate is collected and analyzed by direct aqueous-injection gas chromatography. Detection limits of approximately 1 μg/l (10^{-3} ppm) have been reported for water-soluble volatiles using this method. Poor recoveries render the meth-

TABLE 1
Trap-Saturation Volumes

Compound	Silica Gel Layer *ml*	Pora Pak Q *ml*	Chromosorb 103 *ml*	Tenax GC *ml*	Retention Index
Methane	<5*	<5*	<5*	†	100
Ethane	<25*	<5*	<5*	‡	200
Propane	>50*	<50*	<10*	‡	300
n-Butane	>500*	<100*	<20*	‡	400
n-Pentane	>500*	<250†	<50†	‡	500
n-Hexane	>500*	>500†	>500†	>500†	600
n-Alkanes C_7–C_{15}	‡	>500†	>500†	>500†	700–1 500
Benzene	>500*	>500‡	>500†	>500†	–
Toulene	>500*	>500†	>500†	>500†	–
Methylene chloride	‡	>500§	>500§	>500§	–
Chloroform	‡	>500§	>500§	>500§	–
Aldehydes C_2 and above	Nonquantitative	>500*	>500*	‡	–
Phenols	‡	>500*	>500*	‡	–
Naphthylene	‡	>500*	>500*	‡	–
Chlorobenzene	‡	‡	>500§	>500§	–
o-Dichlorobenzene	‡	‡	>500§	>500§	–
1,2,4 Trichlorobenzene	‡	‡	>500§	>500§	–

*Values reported by Bellas and Sigsby [9]
†Values determined using water-saturated nitrogen as purge gas are same as those reported under dry conditions.[9]
‡Not determined
§Determined for this study

TABLE 2
Purging of Selected Compounds From Water

Nitrogen Purge Gas		Percentage Remaining in Aqueous Phase			
Flow Rate *ml/min*	Volume *ml*	Methylene Chloride	Chloroform	Benzene	2-Butanone
20	0	100	100	100	100
20	20	60	55	46	95
20	100	0	0	3	96
20	300	0	0	0	80
13	0	100	100	100	100
13	6.5	67	94	71	100
13	85	30	29	6	86
13	143	6	0	0	74
			Solubility in water—*per cent*		
		2	1	0.08	35
			Boiling point—*C*		
		40.1	61.3	80.1	79.6

TABLE 3
System Response to Methylene Chloride

Concentration *µg/l*	Slope 0,0 to Data Point	Dilution
5.2	78.5	1/100
10.4	76.9	2/100
20.8	78.5	5/100
52.0	77.5	10/100
104.0	76.3	20/100
260.0	72.9	50/100
520.0	85.7	Stock solution
	78.0 mean	
	3.88 std. dev.	

od useless for water-insoluble components.

The head-gas technique[8] in which a sample is sealed in a partially filled container, has been employed for many years. Each volatile organic compound establishes an equilibrium between the gaseous and aqueous phase. At low concentrations the ratio of the concentration in the gaseous phase to the concentration in the aqueous phase is a constant (partition coefficient) and is unique for each organic compound. By analyzing the gaseous phase and applying the appropriate partition coefficient, one can calculate the concentration of each organic initially present in the aqueous phase.

Of the techniques previously mentioned, the head-gas method has the greatest potential for meeting the needs set

TABLE 4
System Response to Chloroform

Concentration *µg/l*	Slope 0, 0 to Data Point	Dilution
6.2	32.3	1/100
12.4	29.7	2/100
24.8	28.1	5/100
62.0	26.8	10/100
124.0	26.8	20/100
310	25.4	50/100
620	29.9	Stock solution
	28.4 mean	
	2.35 std. dev.	

TABLE 5
System Response to Benzene

Concentration *µg/l*	Slope 0, 0 to Data Point	Dilution
3.5	220.6	1/100
7.0	219.4	2/100
14.0	214.9	5/100
35.0	215.8	10/100
70.0	207.5	20/100
175	196.0	50/100
350	232.0	Stock solution
	215.2 mean	
	11.4 std. dev.	

TABLE 6
System Response to Toluene

Concentration *µg/l*	Slope 0, 0 to Data Point	Dilution
3.5	120	1/100
7.0	120	2/100
14.0	116	5/100
35.0	115	10/100
70.0	111	20/100
175.0	105	50/100
350.0	124	Stock solution
	116 mean	
	6.27 std. dev.	

TABLE 7
Purging Efficiency at 19.5 C, Percentage Recovery

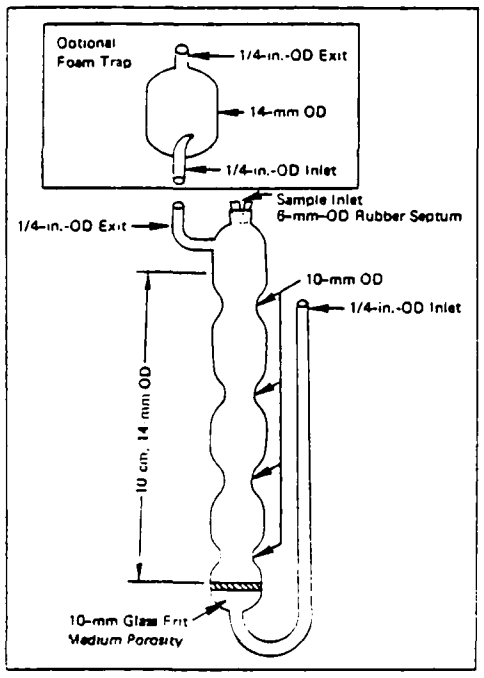
Purge Volume *ml N_2*	Compound and Boiling Point							
	n-C_5 *36C*	n-C_6 *69C*	n-C_7 *98C*	n-C_8 *126C*	n-C_9 *150C*	n-C_{11} *196C*	n-C_{13}* *234C*	n-C_{15}* *270C*
0–60	100	100	98	90	76	60	44	2
60–120			2	6	12	15	17	13
120–240				3	8	9	13	27
240–360				1	3	4	6	14
360–480					1	2	3	3
480–600						2	5	7
600–720						2	3	5
720–840						1	2	5
840–960						1	2	4
960–1 080						1	2	4
1 080–1 200						2	2	7

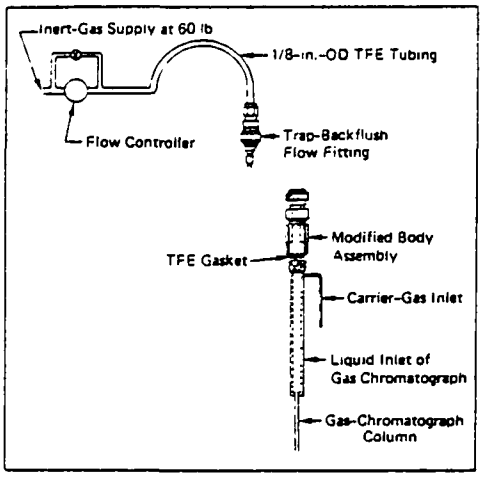
*Not 100 per cent purged using 1 560 ml N.

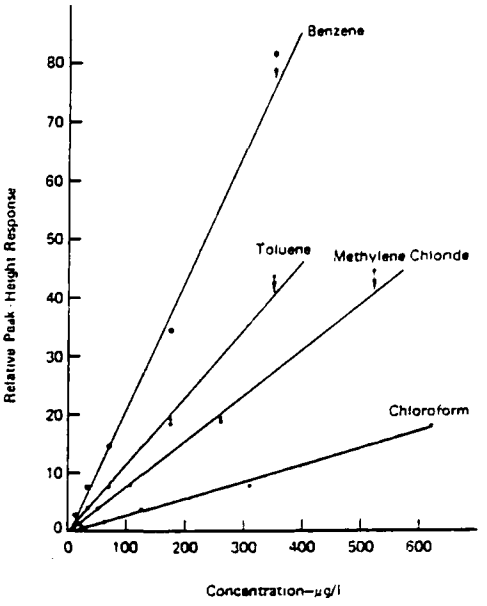
TABLE 8
Purging Efficiency at 65C, Percentage Recovery

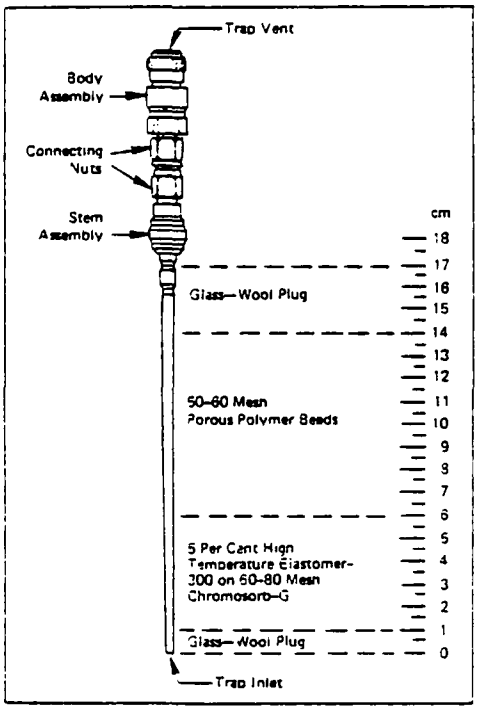
Purge Volume *ml N_2*	Compound and Boiling Point							
	n-C_5 *36C*	n-C_6 *69C*	n-C_7 *98C*	n-C_8 *126C*	n-C_9 *150C*	n-C_{11} *196C*	n-C_{13}* *234C*	n-C_{15}* *270C*
0–60	100	100	100	100	97	76	66	27
60–120					3	10	12	24
120–240						6	6	15
240–360						4	6	11
360–480						2	4	7
480–600						1	3	6
600–720						1	2	6
720–840							1	4

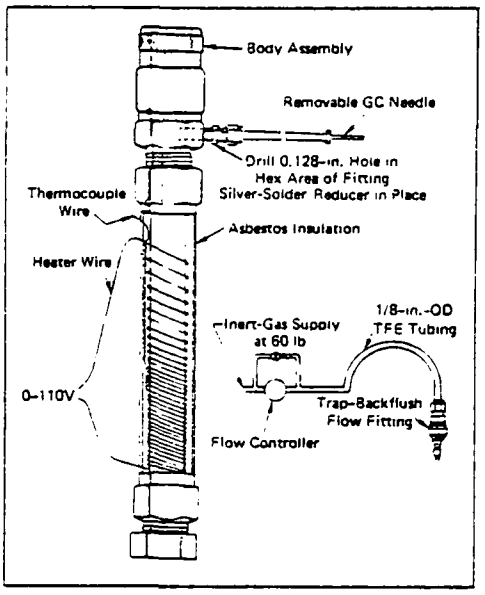
*Not 100 per cent purged

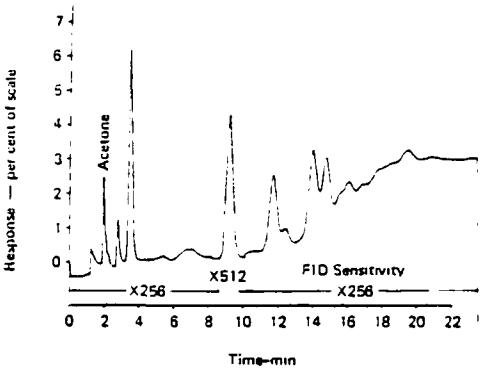












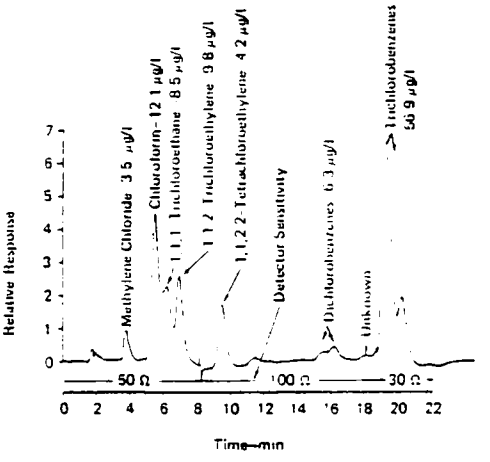


Fig. 1. (Top left) Diagram of Purging Device; **Fig. 2.** (Bottom left) Schematic of Trap; **Fig. 3.** (Top center) Diagram of Desorber 1; **Fig. 4.** (Bottom center) Diagram of Desorber 2; **Fig. 5.** (Top right) Response Curves for Selected Organic Compounds; **Fig. 6.** (Right center) Chromatogram of Effluent Using Desorber 1 and Flame-Ionization Detector; **Fig. 7.** (Bottom right) Quantitative Identifications of Effluent Using Desorber 1 and Microcoulometric Detector

forth in the *Fed. Rgtr.*[1] In order for this method to be effective, the following steps must be followed:

1. Transfer of 95–100 per cent of the organics contained in the aqueous phase into the gaseous phase
2. Quantitative injection of all of the organics contained in the gaseous phase into a gas chromatograph

If these are done, 5.0 ml (0.3 cu in.) of aqueous sample will be sufficient to provide a method sensitive to 1.0 µg/l (10^{-3}ppm); this sample size is based upon the average limit of detection for direct aqueous-injection techniques.

Since, in a static system, it is impossible to alter the partition coefficient to favor the gaseous phase 100 per cent, the study of a dynamic system was initiated whereby a sweep (purge) gas is bubbled through the sample until the volatile organics are quantitatively transferred to the gaseous phase. The organics that are quantitatively transferred to the gaseous phase could then be concentrated for gas-chromatographic analysis with the use of a noncryogenic trapping technique developed a number of years ago for ambient-air[9] and dilute-emission analysis.[10] In this manner an analysis performed upon the gas phase would have a direct relationship to the aqueous-phase concentration.

Experimental

Apparatus. Several pieces of commercial equipment must be slightly modified and assembled to meet the needs of the method.*

Purging device. The purging device (Fig. 1) is constructed from glass tubing. The glass frit installed at the base of the sample reservoir allows finely divided gas bubbles to pass through the aqueous sample while the sample is restrained above the frit. The sample reservoir is designed to provide

*Equipment specifications may be obtained by writing the JAWWA editorial staff or the authors. Methods Dev. and Qual. Assurance Res. Lab., USEPA, Natl. Envir. Res. Ctr., Cincinnati, Ohio 45268.

maximum bubble contact time and efficient mixing.

Gaseous volumes above the sample reservoir are kept to a minimum to provide efficient transfer characteristics and allow sufficient space in which most foams can disperse. Inlet and exit ports are constructed from 0.06-mm (1/4-in.)-OD medium- or heavy-wall tubing so that leak-free removable connections can be made using "finger-tight" compression fittings containing plastic ferrules. The optional foam trap is used to control occasional samples that foam excessively.

Trap. The trap (Fig. 2) is a short section of stainless-steel tubing packed with an adsorptive material such as gas-chromatographic grade porous polymers, silica gel, or molecular sieve. Volatile materials are transported directly from the purging device into the trap by the purge gas. The adsorbent retards the flow of the purged compounds while the purge gas is vented. The properties of the adsorptive material are chosen to meet the needs of the particular analysis. The following criteria must be met.

The volume of the purge gas passing through the adsorbent packed in the trap can approach but not reach the retention volume of the compound to be trapped (See Table 1).

The retained compounds must not be irreversibly sorbed by the trap. (Silica gel irreversibly adsorbs some aromatics above C_9).[9]

No chemical reactions or rearrangements may take place when the sample is being concentrated, stored, or desorbed. (Silica gel causes externally bonded olefins to rearrange to the cis- and trans-2 olefins).[9]

The adsorptive material must be thermally stable. Chromosorb 103 and Tenax GC have been found to perform satisfactorily. (Divinyl benzene crosslinked porous polymers out-gas extraneous compounds causing serious interferences during most gas-chromatographic analyses.)[10]

The trap is assembled and packed with the appropriate adsorptive material according to Fig. 2. The body assembly acts as a seal for the exit end of the trap. The modified stem assembly is used to attach the trap to the desorption device. The cap is used to seal the inlet end of the trap when it is not in use.

Desorbers. The desorbers (Fig. 3, 4) are used to transfer the contents of the trap to the gas chromatograph for analysis. This is done with the use of an auxiliary carrier flow-control system which backflushes the trap at elevated temperatures directly onto the gas-chromatographic column. Desorber 1 is used exclusively with one type of gas chromatograph, but desorber 2 can be used as a universal desorber for all gas chromatographs with a septum-type liquid-inlet system.

Desorber 1 (Fig. 3) is attached directly onto the gas-chromatograph liquid-inlet system after removing the septum nut, the septum, and the internal injector parts. The modified body assembly is screwed onto the inlet system using the TFE gasket as a seal. A plug is attached to one of the stem assemblies. The assembled parts, simply called "the plug," are used to seal the desorber whenever the trap is removed to maintain the flow of carrier gas through the gas-chromatographic column. The flow controller, TFE tubing, and stem assembly are used to provide the trap-backflush flow. This entire assembly is also used to provide gas flow to operate the purging device.

Desorber 2 (Fig. 4) may be attached to any gas chromatograph by piercing the GC liquid-inlet septum with the needle. The desorber is assembled according to Fig. 4 with internal volumes and dead-volume areas held to a minimum. The heat source is concentrated near the base of the desorber so that the internal seals of the body assembly do not become damaged by heat. The use of a detachable needle assembly from a microsyringe makes it easy to replace plugged or dulled needles. The flow controller, TFE tubing, and stem assembly are used to provide the trap-backflush flow. This entire assembly is also used to provide gas flow to operate the purging device.

A gas chromatograph was equipped with dual-flame ionization detectors and a microculometric detector (halide mode).

Column 1 consisted of dual, stainless-steel, 180-cm (6-ft) long × 2.67-mm (0.105-in) ID columns, packed with Chromosorb-101 (60/80 mesh). The carrier gas was nitrogen at 50 ml/min (0.cu ft/hr). The oven temperature was isothermal 190C (310F) or programmed from 120C to 225C (247F to 437F) at 10C (50F)/min.

Column 2 consisted of dual, stainless-steel, 91-cm (3 ft) × 1.65-mm- (0.065-in.)- ID columns packed with 4 per cent SE-30 on Chromosorb-P (NAW) (60/80 mesh). The carrier gas was nitrogen at 50 ml/min (0.1 cu ft/hr). The oven temperature was programmed from 60C to 230C (140F to 446F) at 10C (50F)/min.

The GC-MS system consisted of a gas chromatograph* with a mass spectrometer† controlled by a data-acquisition system.‡ The column was glass, 240-cm (8-ft) long × 2-mm (0.078-in.) ID and packed with Chromosorb-101 (50/60 mesh). The carrier gas was helium at 30 ml/min (0.06 cu ft/hr). The initial oven temperature was 125C (257F) for 3 min and then programmed at 4C (39F)/min to 220C (428F).

Reagents

Organic-free water was prepared by passing distilled water through a water-treatment system.§

Standard stock solutions were prepared by injecting 1-5 μl 61.02×10^{-6} cu. in. of the compound to be determined into a 1-1 (61-cu in.) volumetric flask partially filled with organic-free water. The mixture was then diluted to volume with organic-free water to give concentrations between 1 and 7 mg/l (1 and 7 ppm). Dilutions were made from the stock solution by pipetting a known quantity of stock solution into a partially filled volumetric flask and diluting to volume with organic-free water. [For low-level work (1-10 μg/l) (10^{-3}–10^{-2}ppm) a 1:10 dilution of the stock solution was prepared, and secondary dilutions were prepared.]

Procedure

Purging and trapping. With nitrogen gas flowing through the purging device (Fig. 1) at 20 ml/min (0.04 cu ft/hr), the trap inlet (Fig. 2) was attached (finger-tight) directly to the purging device exit using a compression fitting. The trap vent was inserted into the exit end of the trap. Five millilitres of sample were injected into the purging device and purged for the specified time (11 min). The trap was then removed from the purging device, and the vent plug was removed and replaced with a cap to seal the trap inlet.

Trap conditioning. Newly packed traps were conditioned at approximately 200C (392F) with a nitrogen flow of 20 ml/min (0.04 cu ft/hr) for 16–24 hr with one of the desorbers and vented to the room. Prior to daily use, traps were placed into the desorber and conditioned at 130C (266F) for approximately 10 min while being backflushed with nitrogen at 20 ml/min (0.04 cu ft/hr).

Desorption and analysis. *Desorber 1* (Fig. 3). The gas-chroma-

*Varian Aerograph Ser. 1400
†Finnigan 1015C Quadrupole
‡Systems Industries 150
§Millipore Super-Q

tographic oven was cooled to below 30C (86F) by leaving the oven door open. The plug was removed from the desorber, and the cap was removed from the trap; the trap was then inserted into the desorber and locked into place. The trap-backflush flow fitting was then locked into place on the trap-exit flow fitting and backflushed with nitrogen at 20 ml/min (0.04 cu ft/hr) for 3 min between 125C and 130C (257F and 266F). The trap-backflush flow fitting was removed with the trap still locked into place, the oven lid was closed, and the oven was rapidly heated to its normal or initial operating temperature. A gas-chromatographic analysis was carried out under these conditions.

After analysis the trap was removed by: (1) inserting the trap vent into the trap-exit fitting (to vent-inlet system), (2) removing the trap, (3) resealing GC-inlet system with the plug, (4) removing the trap vent, and (5) resealing the trap inlet with the cap.

Desorber 2 (Fig. 4). The gas-chromatographic oven was cooled to below 30C (86F). The needle was inserted into the liquid-inlet system on the gas chromatograph. The trap was then inserted into the desorber and locked into place. The trap-backflush flow fitting was locked into the trap-exit flow fitting and backflushed with nitrogen at 20 ml/min (0.04 cu ft/hr) for 3 min between 125C and 130C (257F and 266F). After desorption and sample transfer were completed, the needle was removed from the liquid-inlet system, the oven lid was closed, and the oven was rapidly heated to the initial operating temperature. Gas-chromatographic analyses were performed under these conditions. After sample transfer the trap was removed and sealed for future use.

Investigation of Method Parameters

Initial studies were carried out to determine the volume of purge gas needed for quantitatively extracting selected volatile materials from a water sample. The purging device was charged with 5.0 ml (0.3 cu in.) of an aqueous solution containing methylene chloride, chloroform, benzene, and 2-butanone concentrations, each in excess of 10 mg/l (10 ppm).

As the solution was being purged with nitrogen, 3-μl aliquots were periodically withdrawn for analysis by direct-aqueous injection. Analyses were performed on the aqueous mixture until the concentrations of the dosed materials were reduced to or below the limit of detection, approximately 100 μg/l (10^{-1} ppm). This experiment was initially performed with a purge-gas-flow rate of 20-ml/min (0.04-cu ft/hr) nitrogen. The flow rate was reduced 65 per cent to 13 ml/min (0.03 cu ft/hr), and the experiment repeated. The percentages of the dosed compounds remaining in the aqueous phase with respect to the purge volume are listed in Table 2.

Those trap saturation volumes reported in Table 1, designated by footnote †, were obtained by Bellar and Sigsby[9] for a dry-air system. To determine what effect, if any, water that is inherent to the system reported herein, would have on the saturation volumes, the authors redetermined the volumes using water-saturated nitrogen as the purge gas; little if any, change was observed. The saturation volumes for several organochlorine compounds, not previously reported, were also determined under this condition.

The purging-and-trapping system was tested with selected industrial solvents over a wide range of concentrations. Ideally the response for each compound would be linear over the entire concentration range. By using the standard solutions and operating parameters previously described, the authors obtained the data listed in Tables 3–6. The peak height of each compound was measured and divided by the concentration to give the slope between 0,0 and each data point collected. Response curves for four common organic solvents are shown in Fig. 5. The standard deviations from the mean slope are also listed in the tables.

To determine the effect of variation in the physical properties of individual compounds on the efficiency of the system, the authors tested a homologous series of n-alkanes. The test mixture consisted of n-C_5 to n-C_{15} in organic-free water. This mixture was analyzed according to the prescribed procedure using a Tenax trap. Tenax was used as the adsorbent because it has a higher thermal stability than Chromosorb 101 and can be operated at the temperatures required for desorbing the higher molecular-weight alkanes. To determine the purge volume required for quantitative transfer of hydrocarbons over the wide boiling range, successive fractions were collected at ambient temperature (19.5C) [67F] and analyzed by flame ionization (FID) gas chromatography using an SE-30 column (See Table 7). The test was repeated at an elevated purging temperature (65C) [149F] (Table 8).

When the method was applied to a sample from a local sewage plant which serves a diverse industrial area, the complicated FID gas chromatogram shown in Fig. 6 resulted. The sample was analyzed again using the microcoulometric detector which gave the chromatogram shown in Fig. 7. The compounds identified in the chromatograms were confirmed by GC-MS.

Results and Discussion

The data in Table 2 show that it is possible to purge the water insoluble (<2 per cent soluble) compounds from 5 ml of water using < 150 ml (9 cu in.) of nitrogen. A decrease in the purge-gas flow rate of 65 per cent indicated that a slight increase in the volume of purge gas is needed for quantitative transfer. Water-soluble materials whose partition coefficients do not favor the gaseous phase are only qualitatively transferred regardless of the purge volume.

Trapping. Judging from the data reported by Bellar and Sigsby[9] and other data exhibited in Table 1, one can see that organics contained in small volumes of water-saturated nitrogen can be concentrated. It is apparent from these data that compounds with a retention index > 500 can be quantitatively purged and trapped. Retention indices given in the literature on porous polymers[11-13] make it possible to predict trap saturation volumes for a wide variety of organic compounds. Since most hydrocarbons and substituted hydrocarbons commonly present in wastewaters have retention indices >500, porous polymers were used in developing this method.

Water has a retention index of < 300 and is not quantitatively trapped by porous polymers. Therefore, gas-chromatographic columns and detectors adversely affected by water can be used with a minimum of interference.

The statistical data generated in Tables 3–6 reflect an accumulation of errors for the entire method. After one considers the number of manipulations involved and that gas-chromatographic errors are generally ±3 per cent, it appears that this is, indeed, a useful method. Further study of these data indicates that the majority of the errors are caused by the volumetric-dilution procedure. The larger the pipet used to withdraw aliquots of the stock solution, the larger the error. A buret may be a more suitable device for delivering volatile solutes.

For the compounds studied, based on data in tables 2-6, the authors estimated that purging transferred at least 99

p.. cent of the volatile, water-insoluble compounds from the aqueous phase to the gaseous phase. The data in Tables 3–6 and some unreported duplicate data show that the purging efficiency is identical from 2 500 μg/l (2 500 × 10^{-3} ppm) to at least 6 μg/l (6 × 10^{-3} ppm). Therefore, the compounds studied can be quantitatively determined over that concentration range.

Further study of the data in Table 7 indicates that the alkanes up to C_9 can be quantitatively purged using < 500 ml (30 cu in.) of purge gas. Purge volumes exceeding 1.5 l (91.5 cu in.) failed to transfer 100 per cent of the C_{11} through C_{15} alkanes. Raising the temperature of the purging device and sample (Table 8) extended the useful range of the method to C_{11} hydrocarbons. If a water sample contains volatiles over the entire boiling range represented by these data, it may be necessary to trap two fractions in order to perform a complete quantitative analyses on the sample. This is apparent from the data in Table 1 that show that compounds with a retention index of < 600 will saturate the trap and be vented before the high boiling materials are quantitatively purged.

Sample preservation. Because of the volatility of the organic materials detected by this method, common sample-preservation techniques are inadequate.[3,4] The simplicity of the trap-and-purging device makes it possible, however, to collect, purge, and trap the sample at the sampling site. The trap and contents can then be sealed and shipped to the laboratory for analysis, and thus, the need for sample preservation is eliminated.

Application of the method. Judging from the experimental data reported in this article, one may see that this method has great potential for the analysis of trace-volatile organics contained in a wide variety of water sources. For quantitative determinations the method is limited to organic compounds that are < 2 per cent soluble in water and boil below 200C (392F). Significant qualitative enhancement of compounds whose boiling points exceed 200C (392F) can be expected when the sample is heated. The method is useful from 1 to 2 500 μg/l (10^{-3} to 2 500 × 10^{-3} ppm) with the use of most gas chromatographs. At concentrations exceeding 2 500 μg/l (2 500 × 10^{-3} ppm) chromatograph-column flooding and nonlinear-detector responses generally occur. Since direct-aqueous injection techniques are useful down to 1 000 μg/l (1 000 × 10^{-3} ppm) the two methods can be used together to perform analyses over a wide range of concentrations. For water-soluble compounds the distillation technique should provide the supplemental methodology needed to analyze most industrial effluents and natural waters.

A wide variety of wastewater samples were analyzed using the described method. The chromatograms (Fig. 6, 7) show the results of one such analysis. Qualitative identifications were made using desorber 2 and a GC–MS system.* The quantitative analyses were obtained using desorber 1 with a microcoulometric detector. Only one of the peaks in the FID chromatogram have been identified. At the sensitivity ranges shown, only the chlorobenzenes are likely to appear on the FID chromatogram.

The method worked well except for the following: one sample collected from a sewage-treatment plant foamed excessively and caused water to be transported from the purging device into the trap. Decreasing the sample size from 5 to 3 ml (0.3 to 0.2 cu in.) or using the foam trap eliminated this problem. Water entering the trap causes nonquantitative trapping and severe gas-chromatographic interferences.

When water samples contained gross amounts of water-soluble organics, a sufficient quantity of these materials was collected in the trap for detection. When only water-insoluble materials were present in the sample, it was found that the purged water could be withdrawn with a syringe and the purging device could be recharged for successive analyses. When large concentrations of water-soluble organics were present, it was necessary to dry the purging device in an oven at 110C (230F) before an interference-free successive analysis could be performed. Other researchers[14,15] have reported on similar methods for the analysis of aqueous samples; their work has been primarily qualitative.

This current work has shown that the method can be used for the quantitative measurement of a wide variety of water-insoluble compounds whose boiling points are < 150C (302F). By slightly modifying the method, one can also quantitatively measure materials that boil at approximately 200C. Qualitative sample concentration occurs for a wide variety of other materials for which quantitative measurements could possibly be made if recovery factors were experimentally determined. Vinyl chloride is one compound of considerable interest that can be determined by this method. Analytical conditions for this specific application are under investigation.

Summary

The method for quantitative recovery and gas-chromatographic determination of water-insoluble, volatile organic compounds presented here provides a detection limit of approximately 0.5 μg/l for many compounds.

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*Finnigan System

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REFERENCE NO. 2

REFERENCE COMPOUND TO CALIBRATE ION ABUNDANCE MEASUREMENTS IN GAS CHROMATOGRAPHY--MASS SPECTROMETRY SYSTEMS

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Reference Compound to Calibrate Ion Abundance Measurements in Gas Chromatography–Mass Spectrometry Systems

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Gas chromatography–mass spectrometry (GC/MS) data from several surveys pointed out the need for a standard procedure for calibration of the ion abundance scale in GC/MS systems. In addition, there is a need for a standard test to evaluate the overall performance of these systems. A number of proposed reference compounds were evaluated with respect to a set of criteria for an ideal GC/MS reference compound. The compound decafluorotriphenylphosphine (DFTPP) was selected because its properties best satisfied the criteria. A set of standard relative abundance ranges for DFTPP were developed by examination of GC/MS data obtained on a variety of systems. Computerized data systems were considered an integral part of the GC/MS system for both ion abundance calibrations and performance evaluations.

Historically, the calibration of the mass/charge and ion abundance scales in mass spectrometry has been a user responsibility. Unlike some other forms of spectrometry, manufacturers of mass spectrometers (MS) could not and did not provide precalibrated chart paper. With the introduction of computerized systems, automatic calibration programs were developed for the mass/charge scale. These programs are based on the use of a reference material, usually perfluorotributylamine (PFTBA) or perfluoro kerosine (PFK), which have well defined ions at specific masses.

With the computerized systems, ion abundance measurement calibrations remained a user responsibility. Several different types of mass spectromters, i.e., magnetic, radio frequency (RF, quadrupole), and time-of-flight, are in widespread use as gas chromatography (GC) detectors, and variations in abundance measurements can be very large. There is a clear need for a standard calibration procedure to provide a reasonable basis for comparison of output from the large variety of equipment in use. In addition, a standard ion abundance calibration would support the increasingly heavy reliance on files of reference spectra to make empirical identifications of compounds in environmental, biomedical, and other types of samples. Clearly, correct identifications require some consistency between reference spectra and observed spectra, and better quality abundance data would improve the effectiveness of all empirical search systems.

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In addition to an ion abundance calibrant, there is a need for a reference compound to evaluate the overall performance of a computerized GC/MS system. We have observed spectra with acceptable ion abundances but, because of poor resolution adjustment, broad peaks that were interpreted by the data system as multiplets. A reference procedure would allow an operator to validate the performance of the GC column, the sample enrichment device, the ion source, the ion detection circuits, the analog-to-digital converter, the data reduction system, and the data output system. The application of this procedure would enhance the overall quality of results emerging from the systems in use.

There is a special need to closely monitor the performance of the RF quadrupole mass spectrometer. Unlike the magnetic deflection spectrometer, the active ion separating device of the RF field spectrometer, the rods, is directly contaminated during operation. After prolonged operation, the rods are subject to severely degraded performance which usually affects the region above 300 amu first. Often this degraded performance is not detected because there is no generally accepted performance standard to form the basis for such judgments.

The Environmental Protection Agency has developed and used experimentally a performance evaluation/abundance calibration procedure for the last several years. A set of chemical and physical properties criteria for a reference material was developed and a number of likely candidates, including PFK and PFTBA, were tested. The compound decafluorotriphenylphosphine (DFTPP) was selected as the one which met most of the criteria.

This paper reports the criteria on which the compound was selected, its mass spectrum, some physical and chemical properties, and some performance data that were collected over the last few years. An RF field mass spectrometer, which has been tuned to give the suggested ion abundances in the reference compound spectrum will, in general, generate mass spectra of organic compounds which are very similar to spectra generated by other types of mass spectrometers. Thus RF field mass spectra become directly comparable to spectra of compounds in collections which have been obtained with other types of mass spectrometers.

EXPERIMENTAL

Materials. All chemicals and solvents were obtained from commercial sources. Decafluorotriphenylphosphine was prepared ac-

cording to the procedure of Dua (1); m.p. 62–64°; *Anal.* Calcd for $C_{38}H_{15}F_{30}P$: C, 48.89; H, 1.13. Found: C, 48.95, 49.05; H, 1.10, 1.07. *Purity, based on flame ionization detector gas chromatographic measurements* was estimated at 99.5% or better.

Instrumentation. Mass spectra that were measured in this laboratory were obtained with a Finnigan 1015 RF quadrupole mass spectrometer. The inlet systems were a Varian Series 1400 gas chromatograph and an all-glass batch system with a constant leak opening that introduced the sample directly into the ion source. The chromatograph was interfaced to the spectrometer by an all-glass jet type enrichment device and an all-glass transfer line. Control of the quadrupole rod mass set voltages, data acquisition, data reduction, and data output was accomplished with a System Industries data system which employed a Digital Equipment Corporation PDP-8/E mini-computer and a 1.6 million word Diablo disk drive.

All of the systems referred to in Table III also used this spectrometer and data system which has a user option to integrate ion currents at one or more (maximum of ten) 0.1-amu intervals between each integer mass. The maximum ion current value is selected for each amu by the control program and abundances of non-integer ionic masses are measured correctly. With DFTPP, this option was not used since the ions in the spectrum of DFTPP have masses very close to the integer values (e.g., M^+ = 441.997).

The gas chromatograms and mass spectra were displayed on a Tektronix Model 4010 cathode ray tube or a Houston Instruments model DP-1 flat bed plotter.

Gas Chromatography. Most of the work reported in this paper was carried out using a 6-ft × 2-mm (i.d.) glass column packed with 1.95% QF-1 plus 1.5% OV-17 on 80/100 mesh Supelcoport. The flow rate was about 30 ml/min; column temperature, 180°; injector temperature, 210°; and interface oven-transfer line temperature, 200–210°. The compound decafluorotriphenylphosphine was also chromatographed on a variety of other columns of varying length and stationary phases. In general these were 4–8 ft, metal or glass, 100–250° column temperatures, and 20–35 ml/min flow rates. Stationary phases were 3% SE30, 5.5% OV1, 3–5% OV17, 2–6% OV101, Dexil 300, and 0.1% OV210.

Chromatography was also successful on a 100-ft, 0.02-in. (i.d.) support coated open tubular column coated with QF-1. In general, retention times of 4–10 minutes were observed. Cross-linked porous polymer packed columns were not suitable for this compound. Similarly, a 7-ft coiled glass column (i.d. 2 mm) packed with 10% free fatty acid phase on 60/80 mesh chromosorb W gave poor results.

Procedure. A stock solution of DFTPP at 1 mg/ml (1000 ppm) concentration in acetone was prepared. This stock solution was shown, by repeated analyses, to be 97%+ stable after six months, and indications are it will remain usable for several years. An aliquot of the stock solution was diluted to 10 μg/ml (10 ppm) in acetone. The very small quantity of material present in this very dilute solution is subject to depreciation because of adsorption on the walls of the glass container, reaction with trace impurities in the acetone, etc. Therefore the dilute solution was used for only a short term, i.e., 1–2 weeks.

The gas chromatographic operating parameters were adjusted to permit the acquisition of at least four complete mass spectra during the elution of the DFTPP. The mass/charge scale of the mass spectrometer was calibrated according to the standard procedure provided by the manufacturer. The mass spectrometer and data system were prepared for GC data acquisition using the following parameters: mass range, 33–500 amu; electron energy, 70 eV; trap current, 250–500 μA; preamplifier sensitivity, 10^{-7} A/volt; electron multiplier voltage, 3000 volts; and mass spectrometer manifold temperature, 100°. Under these conditions, the ion source temperature of the Finnigan mass spectrometer is not known. The pressure in the spectrometer was about 10^{-5} Torr and the base line was adjusted with the automatic zero program. The spectrometer data system was set to integrate the preamplifier signal for 8 msec at each integer mass unit. Alternatively, the integration time as a function of signal strength option was utilized. This will be described in detail in a future publication (2).

An injection of 20 ng (2 μl) of the dilute standard was made and data acquisition was begun after most of the solvent was pumped from the spectrometer. Data acquisition was concluded after elution of the DFTPP. The mass spectrum of DFTPP was obtained by selecting a spectrum number on the front side of the GC peak as near the apex as possible. A background spectrum was selected from one of the spectra immediately preceding the DFTPP peak. Several spectra were sometimes plotted in an attempt to find one which fit the abundance criteria. If no spectrum could be obtained which fit the criteria, the rod and ion source potentials were adjusted as in the manufacturer's tune-up procedure. If this failed to produce the correct spectrum, more extensive maintenance was performed. This was usually cleaning the ion source and/or the quadrupole rods. These measures usually corrected the malcondition and a spectrum of DFTPP could be obtained which fit the criteria.

RESULTS AND DISCUSSION

The results of several recent studies illustrate the need for a standard relative abundance calibration procedure and performance evaluation standard. A study was reported in 1973 (3) of calibration data from various types of mass spectrometers. Relative abundance data were reported for an aliphatic hydrocarbon, *n*-hexadecane, and an alkylated aromatic hydrocarbon, 1-phenyl undecane. The participating laboratories introduced these samples with conventional batch inlet systems into a variety of single and double focusing magnetic deflection and several RF quadrupole spectrometers. Selected data from that study are given in Table I. Measurements at the selected ions agree reasonably well below about mass 100. Above mass 100, there is a clear indication of reduced sensitivity with the quadrupole spectrometers. This trend supports the widespread idea that quadrupole spectrometers are significantly less sensitive than magnetic deflection spectrometers at the higher masses. The data above mass 100 obtained with the 21-491 and MS-902 spectrometers reveal the well known fact that magnetic deflection spectrometers are susceptible to reduced high mass sensitivity also. This may be due to emphasis on low mass sensitivity during ion source tuning or performance degradation due to contamination of the ion source.

In late 1972, samples of DFTPP were sent by us to a number of EPA and other laboratories. This survey was conducted to obtain relative abundance comparisons up to mass 450. In addition, it was requested that the sample be introduced with a GC inlet system and any GC column that was convenient for the participating laboratory. The results from magnetic deflection systems are shown in Table II and from RF quadrupole systems in Table III. The ions selected for comparison are spaced at approximately 75 amu intervals up to mass 275 and include, in addition, the molecular ion (M^+) at mass 442 and the molecular ion containing a single ^{13}C atom at mass 443. The theoretical 443/442 percentage is 19.8%.

Relative abundance data for DFTPP from three of the magnetic sector instruments is in very good agreement and all four magnetic instruments produced acceptable values for the $(M^+ + 1)/M^+$ percentage. The relative abundance data from the 21-490 may be an example of ion source tuning to emphasize the molecular ion region or perhaps it merely reflects the selection of a spectrum number too close to the front of the peak. In the latter event, the molecular ion would have been observed after the concentration of the DFTPP in the ion source had increased significantly.

The relative abundance data for DFTPP from the RF quadrupole spectrometers were much less consistent. Laboratory No. 1 reported the base peak as mass 51, laboratories 2–7 reported the base peak as mass 198, laboratory 8 reported the molecular ion as the base peak, and laboratories 9–11 found mass 69 (CF_3^+) as the base peak. The range of abundance measurements at any given mass was generally much larger with the RF quadrupole spectrometers. For example, the three magnetic deflection spectrometers that measured mass 198 as the base peak had a range of 24 relative abundance units at mass 51. The six quadrupoles that measured mass 198 as the base peak had a range of 39

Table I. Selected Relative Abundance Data for Hexadecane Measured with a Variety of Mass Spectrometers[a]

	Relative abundance, %								
Mass	CH-7[b]	RMU-6[b]	21-490[b]	21-491[c]	21-492[c]	21-110B[d]	MS-902[c]	1015[e]	1015[e]
57	100	100	100	100	100	100	100	100	100
71	60	55	73	65	75	72	66	54	60
85	37	40	49	45	52	48	37	32	35
99	12	12	14	12	16	11	10	7	8
113	7	8	9	7	9	7	6	3	4
127	5	7	7	5	6	6	4	2	2
141	4	5	6	3	6	5	2	1	1
155	4	5	5	3	6	5	2	1	1
226	8	12	11	3	11	9	3	1	1

[a] Data taken from Reference 3. [b] Single focusing sector magnetic deflection spectrometer. [c] Double focusing (electrostatic and magnetic fields) modified Nier-Johnson spectrometer. [d] Double focusing Mattauch-Herzog geometry spectrometer. [e] Radio frequency quadrupole spectrometer.

Table II. Selected Relative Abundance Data for DFTPP Measured with Single Focusing Magnetic Deflection Spectrometers and GC Inlet Systems

	Percent relative abundance at mass						
Spectrometer	51	127	198	275	442	443	443/442 × 10^2
Varian CH-7	40	42	100	26	92	20	21.7
Varian CH-5	60	52	100	24	95	19	20.0
Nuclide 1290G	34	37	100	29	86	17	19.8
DuPont 21-490	12	13	34	11	100	21	21.0

Table III. Selected Relative Abundance Data for DFTPP Measured with Finnigan 1015 RF Quadrupole Spectrometers and GC Inlet Systems

	Percent relative abundance at mass						
Lab	51	127	198	275	442	443	443/442 × 10^2
1	100	49	98	20	51	9	17.6
2	81	50	100	13	33	7.5	22.7
3	53	68	100	24	31	5.5	17.7
4	53	48	100	19	64	12	18.8
5	92	55	100	22	57	12	21.0
6	86	40	100	28	56	10	17.9
7	57	43	100	16	48	10	20.8
8	14	19	42	13	100	91	91.0
9	66	80	76	19	47	13	27.7
10	93	57	85	11	20	4	20.0
11	97	85	65	11	2.5	2.5	100.0

units at mass 51. All four magnetic deflection spectrometers produced molecular ion measurements between 86–100%; the quadrupole values for the molecular ion ranged between 2.5–100%. The values of the $(M^+ + 1)/M^+$ percentage from the four magnetic deflection spectrometers had a standard deviation of 0.8%. The same values from the quadrupole spectrometers had a standard deviation of 3% after rejection of the 91% and 100% observations.

The more diffuse nature of the RF quadrupole abundance measurements was probably due to a variety of causes including the presence of generally less experienced operators, the failure of some operators to utilize ion abundance calibration procedures, inadequate ion source or quadrupole rod maintenance, more difficult quadrupole tune-up adjustments, and the selection of spectrum numbers too close to the front or apex of a GC peak.

The hexadecane spectrum was measured in this laboratory with an RF quadrupole after the spectrometer was adjusted to give a DFTPP spectrum similar to that produced by the Varian and Nuclide magnetic deflection spectrometers. The masses and relative abundances that correspond to those in Table I were: 57, 100; 71, 65; 85, 39; 99, 13; 113, 7; 127, 4, and 226, 10.

We concluded that the RF quadrupole spectrometer could be maintained, without unreasonable effort, in a condition that would produce mass spectrometric fragmentation patterns that were very similar to patterns produced by other types of spectrometers. However, it was also clear that a standard relative abundance calibration procedure and performance evaluation standard was required and that use of this standard would benefit users of magnetic deflection spectrometers also.

Criteria for the Ideal Reference Compound. The ideal reference compound should possess a number of important properties. It should be available in very pure form as a crystalline solid. This is necessary to facilitate accurate weighing and the preparation of standard solutions to evaluate GC/MS system sensitivity in terms of signal to noise for a given quantity. The compound should have high kinetic and thermodynamic stability and be soluble in a variety of common organic solvents to facilitate gas chromatography. The material should be very easy to gas chromatograph on a wide variety of columns of differing polarity. This property would encourage its application on whatever column was of particular importance in a given laboratory. The mass spectrum of the compound must display an

abundant molecular or fragment ion near mass 500. This is an extremely important factor since many compounds of environmental and biomedical significance have ions in the 400–500 amu range. The ion must be very abundant in order to easily evaluate the system sensitivity and resolution in the high mass region. The commonly used mass calibration compounds PFK and PFTBA have ions in this region, but these are very inadequate because of their very low relative abundance. For example, a 100% reduction in spectrometer sensitivity at mass 500 is reflected in the spectrum of PFTBA by a change in relative abundance of the mass 502 ion from 2% to 1%. In contrast, the spectrum of the reference standard should not be dominated by a single very abundant ion which tends to saturate the detector and reduce all other ions to very small relative abundances. Most fluorinated aliphatic compounds, e.g., PFTBA and PFK constituents, suffer from the dominance of the mass 69 CF_3^+ ion. An even distribution of ions of even relative abundances over a wide mass range is most desirable. On the other hand, the compound should not possess too many ions which might cloud a spectrum with too much information to allow a fast evaluation of the system performance.

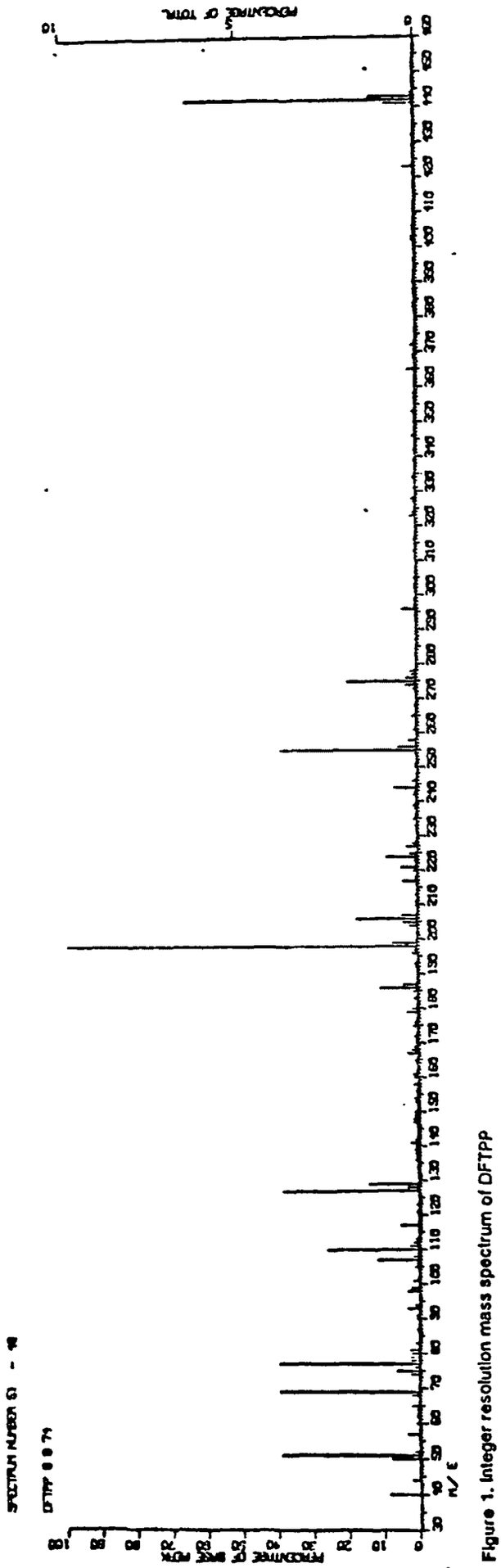
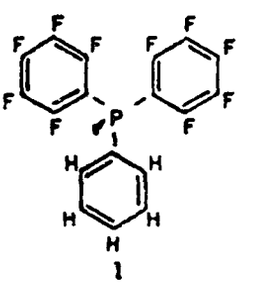


Figure 1. Integer resolution mass spectrum of DFTPP

It was clear that the fluorinated aliphatic compounds including PFK and PFTBA were not suitable because of several serious limitations. *n*-Hexatriacontane is widely used as the standard of reference in hydrocarbon type analyses in the petroleum industry, but its low molecular weight, 226, and the generally low relative abundance of the molecular ions of aliphatic hydrocarbons rule out this type of standard. Cholesterol is a crystalline compound of reasonable molecular weight but it is difficult to chromatograph without derivatization. Methyl stearate is often used as a test compound but it is unacceptable because of its molecular weight, 298, and the low relative abundance of the molecular ion. Perfluorodecalin was recently proposed (*4*) as a mass calibration standard for low resolution mass spectra. One of its attributes is that the relative contribution of mass 69 to the total ionization is much less than for other fluorinated aliphatics. Nevertheless, the compound is a volatile liquid with no ion of greater than 10% relative abundance above mass 293. Perfluoroalkyl-*s*-triazines and related compounds (*5*) have been used to excellent advantage as very high mass calibration standards for the mass to charge scale. They suffer similar disadvantages of dominance by mass 69 and large gaps where no abundant ion is observed. Triphenylnaphthalene (*6*) was reported as a useful mass to charge scale calibrant. This compound has a molecular weight of 356 and produces a large number of ions including several abundant clusters.

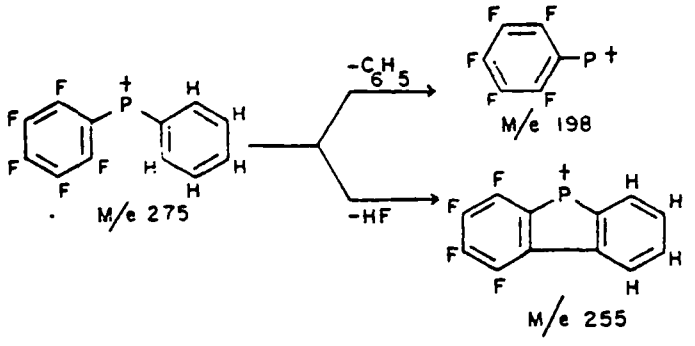
The compound bis(perfluorophenyl)phenylphosphine 1 (or decafluorotriphenylphosphine, DFTPP) was one of a number of compounds evaluated as a possible ion abundance calibration reference compound and standard for performance measurements. Its spectrum is shown in Figure 1. The compound meets nearly all of the criteria described previously. Its spectrum contains relatively abundant ions at about 75-amu intervals (Tables II and III) between masses 51 and 275. It is deficient in that there is no abundant ion in its spectrum between mass 275 and 442. The molecular ion at mass 442 is very abundant but does not dominate, and there are not too many ions that would preclude rapid inspection and evaluation of a spectrometer performance.



1

Proposed Compositions of Ions in the Spectrum of DFTPP. Exact mass measurements and information from decomposition products of metastable ions were not available for DFTPP. Therefore assignments were based on integer mass measurements only and are tentative. Only those ions were included that could be assigned a composition with reasonable assurance that it is correct.

The very small ion at mass 423 results from loss of a single fluorine atom from the molecular ion and the similarly small ion at mass 365 corresponds to loss of a phenyl group. The ion at mass 275 has the composition $(C_6H_5)(C_6F_5)P^+$ which results from the loss of a single perfluorophenyl group from the molecular ion. We propose the fragmentation process in which this ion either loses its phenyl group to form the mass 198 ion, or loses hydrogen fluoride to form the tetrafluorophosphazole ion of mass 255.



Mass 127 is perhaps the phenylfluorophosphine ion $C_6H_5P^+F$. The ions of masses 77, 69, and 51 are well established as the phenyl, CF_3^+, and $C_4H_3^+$ ions. The latter is a decomposition product of the phenyl ion and the CF_3^+ ion is produced by extensive rearrangement of a perfluorophenyl ion.

Relative Ion Abundance Criteria. It was our goal to arrive at a set of relative abundances for DFTPP that would be a standard for performance evaluations and a guide for ion abundance calibration. The data collected in the 1972 survey (Tables II and III) as well as hundreds of repeated measurements in this and several other EPA laboratories were the basis for these criteria. It must be emphasized that the data from the 1972 survey were taken directly from the computer program generated plots or digital printed data when available and that the criteria are intended to apply to the same output. The data handling system of a modern GC/MS is an integrated part of the total system, and the data system performance must be included in the overall evaluation. Clearly, the computer generated output is the most convenient for the operator to use in the evaluation.

The majority of measurements found mass 198 as the base peak and this was selected as the basic criterion (Table IV). All other criteria were developed using only those spectra which had mass 198 as the base peak. Abundant ions were located at approximately 75 amu intervals above and below mass 198. These were masses 51, 127, and 275 and they were included in the criteria to provide a measure of system sensitivity at regular intervals throughout the mass range. The molecular ion at mass 442 and the very scarce ion at mass 365 were selected for the same purpose. Abundant ions at masses 69, 77, 110, and 255 were not used because the selected ions adequately measure system sensitivity. Mass 69 was specifically excluded from the criteria because its abundance frequently depends on background conditions that result from the use of PFK, PFTBA, etc., for mass/charge scale calibrations.

In spectra (Tables II and III) that had mass 198 as the base peak, seven of the nine molecular ion measurements were greater than 40% relative abundance. Therefore, this was selected as a reasonable lower limit for the molecular ion abundance. No upper limit was set. All nine spectra showed an ion of 1–3% at mass 365 and a system with adequate high mass sensitivity should detect at least a 1% ion at this mass. The average abundance for mass 275 in the nine measurements was 22% with a standard deviation (σ) of 5%. This was rather low dispersion for a set of relative abundance measurements and suggests that the abundance at mass 275 is closely related to the arbitrarily constant ion abundance at mass 198. This is consistent with the composition assignments discussed previously. However, a tolerance at mass 275 of ±5% was considered too small for routine GC/MS applications. A criterion at mass 275 of 20 ± 10% was selected by rounding the average relative abundance to the nearest ten percent and allowing a deviation of 2σ. At mass 127, the average abundance in the nine measurements was 48% with σ = 9%. These values were rounded to the nearest ten percent for the criteria, i.e., 50 ± 10%. In the nine measurements, there was considerably more dispersion at mass 51 where the average abundance was 62% and σ = 19%. This was probably caused by the generally higher levels of background hydrocarbon ions present at lower masses in some of the RF quadrupole spectrometers. A tolerance of ±20% was considered too large at this mass. The criteria suggested are 45 ± 15% in order to encourage clean low background systems, yet allow somewhat more tolerance than at higher masses.

Table IV. Reference Compound Key Ions and Ion Abundance Criteria

Mass	Ion abundance criteria
51	30-60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	1% of mass 198
441	Less than mass 443
442	Greater than 40% of mass 198
443	17–23% of mass 442

In addition to sensitivity measurements across the mass range, resolution check points are clearly required. Some computerized data systems interpret broad or poorly shaped peaks as ion abundance where no ions exist. Other systems locate peak centroids and report no ion abundance where ions are present but not completely resolved. In the RF quadrupole spectrometer, improper ion source/rod potentials and ion source magnet orientation causes severe peak skew at the low mass side of a peak which is known as "front end lift off". In Figure 1, front end lift off at mass 69 was interpreted by the data system as ion abundance at mass 68 where no ion exists.

Three resolution check points were chosen to allow an operator to rapidly validate the resolution adjustments as sensed by the data system. In the high mass region the $M^+ - 1$, M^+, and $M^+ + 1$ ions provide a valuable resolution test. For the nine measurements (Tables II and III) that had mass 198 as the base peak, the average value of the $(M^+ + 1)/M^+$ percentage was 20.1 with σ = 1.6. Rounding off and using a 2 σ tolerance gives a reasonable criteria of 20 ± 3% for this percentage. The theoretical value is 19.8%. Repeated measurements have shown that the $M^+ - 1$ ion at mass 441 is always less than the $M^+ + 1$ ion at mass 443.

In the mid and low mass ranges, similar resolution checks were developed using ions containing a single ^{13}C ion at masses 199 and 70. In each instance, the ions are very likely assigned the correct composition and the theoretical percentages may be compared with the experimental. At mass 199, nine measurements gave an average of 8.0% and σ = 2.3. The criterion suggested is 7 ± 2% which compares with the theoretical value of 6.6%. At mass 70, the theoretical value is 1.1%, but most of the nine measurements gave near zero values for this ion. Perhaps this was caused by very slight changes in the base-line (threshold) adjustments. It is very difficult to make accurate and precise measurements of relatively non-abundant ions when observing very small amounts (≃20 ng) in fast (3–4 sec) spectrometer scans. Therefore, for mass 70, we suggest a nominal criterion of less than 2% of mass 69. This is mainly a check on excessive broadness or poor peak shape in the low mass region for those data systems that interpret broadness as ion abundance.

Because of the probable compositions of the mass 198 ($C_6F_5P^+$) and mass 69 (CF_3^+) ions, it is unlikely that mass 197 and mass 68 ions would be present. Indeed repeated measurements have shown that they are not present. Therefore, we suggest that mass 197 should be less than 1% of the base peak, and mass 68 less than 2% of mass 69. Both criteria are checks on excessive broadness and skew as discussed above.

CONCLUSION

The set of relative abundance ranges proposed for DFTPP has been very useful in evaluating the performance of a number of GC/MS systems. These ranges are the basis for the proposed standard ion abundance calibration and provide a reasonable basis for comparing the output from the wide variety of systems in use.

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REFERENCE NO. 3

MEASURING VOLATILE ORGANIC MATTER IN WATER BY AQUEOUS-INJECTION GAS CHROMATOGRAPHY

Designation: D 2908 – 74

Standard Recommended Practice for MEASURING VOLATILE ORGANIC MATTER IN WATER BY AQUEOUS-INJECTION GAS CHROMATOGRAPHY[1]

This Standard is issued under the fixed designation D 2908; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope

1.1 This recommended practice covers the general considerations for the qualitative and quantitative determination of volatile organic constituents in water by gas-liquid chromatography (1,2,3,4).[2,3]

1.2 Direct aqueous injection of samples is feasible at organic concentrations greater than 1 mg/liter. The applicability of the method can be extended to waters of lesser concentrations by evaporative techniques, freeze-out, solvent extraction, or carbon adsorption.[4]

2. Significance

2.1 The major organic constituents in industrial waste water need to be identified for support of effective in-plant or pollution control programs. Currently the most practical means for tentatively identifying and measuring a range of volatile organic compounds is gas-liquid chromatography. Positive identification requires supplemental testing (for example, multiple columns, speciality detectors, spectroscopy, or a combination of these techniques).

3. Summary of Method

3.1 This recommended practice defines the applicability of various columns and conditions for the separation of naturally occurring or synthetic organics or both, in an aqueous medium for subsequent detection with a flame ionization detector. After vaporization, the aqueous sample is carried through the column by an inert carrier gas. The sample components are partitioned between the carrier gas and a stationary liquid phase on an inert solid support. The column effluent is burned in an air - hydrogen flame. The ions released from combustion of the organic components induce an increase in standing current which is measured. Although this method is written for hydrogen flame detection, the basic technology is applicable to other detectors if water does not interfere.

3.2 The elution times are characteristic of the various organic components present in the sample, while the peak areas are proportional to the quantities of the components. A discussion of gas chromatography is presented in ASTM Recommended Practice E 260, General Gas Chromatography Procedures.[5]

4. Definitions

4.1 The following terms in this recommended practice are defined in accordance with ASTM Definitions D 1129, Terms Relating to Water[6]:

4.1.1 *"ghosting" or memory peaks*—an interference, showing as a peak, which ap-

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[1] This recommended practice is under the jurisdiction of ASTM Committee D-19 on Water.

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[2] The boldface numbers in parentheses refer to the references appended to this recommended practice.

Refer also to ASTM Method D 2480, Test for Phenols in Water by Gas-Liquid Chromatography, which appears in this publication.

[3] For information on two of these concentration techniques, refer to ASTM Method D 2778, Solvent Extraction of Organic Matter from Water and ASTM Recommended Practice D 2910, Removal of Organic Matter from Water by Activated Carbon Adsorption, both of which appear in the *1974 Annual Book of ASTM Standards*, Part 31.

[4] *1974 Annual Book of ASTM Standards*, Part 42.

[5] *1974 Annual Book of ASTM Standards*, Part 31.

pears at the same elution time as the organic component of previous analysis.

4.1.2 *internal standard*—a compound of known behavior added to a sample to facilitate the analyses.

4.1.3 *noise*—an extraneous electronic signal which affects baseline stability.

4.1.4 *retention time*—the time that elapses from the introduction of the sample until the peak maximum is reached.

4.1.5 *relative retention ratio*—the retention time of the unknown component divided by the retention time of the internal standard.

4.2 For definitions of other terms used in these methods, refer to ASTM Recommended Practice E 355, Gas Chromatography Terms and Relationships.[5]

5. Interference

5.1 *Particulate Matter*—Particulate or suspended matter should be removed by centrifugation or membrane filtration if components of interest are not altered. This pretreatment will prevent both plugging of syringes and formation of condensation nuclei. Acidification will often facilitate the dissolving of particulate matter, but the operator must determine that pH adjustment does not alter the components to be determined.

5.2 *Identical Retention Times*—With any given column and operating conditions one or more components may elute at identical retention times. Thus a chromatographic peak is only presumptive evidence of a single component. Confirmation requires analyses with other columns with varying physical and chemical properties or spectrometric confirmation of the isolated peak or both.

5.3 *Acidification*—Detection of certain groups of components will be enhanced if the sample is made neutral or slightly acidic. This may minimize the formation of nonvolatile salts in cases such as the analysis of volatile organic acids and bases and certain chlorophenols.

5.4 *Ghosting*—Ghosting is evidenced by an interference peak that occurs at the same time as that for a component from a previous analysis but usually with less intensity. Ghosting occurs because of organic holdup in the injection port. Repeated water washing with 5-μl injections between sample runs will usually eliminate ghosting problems. The baseline is checked at maximum sensitivity to assure that the interference has been eliminated. In addition to water injections, increasing the injection port temperature for a period of time will often facilitate the elimination of ghosting problems.

5.4.1 *Delayed Elution*—Highly polar or high boiling components may unpredictably elute several chromatograms later and therefore act as an interference. This is particularly true with complex industrial waste samples. A combination of repeated water injections and elevated column temperature will eliminate this problem. Back flush valves should be used if this problem is encountered often. Carrier gas wetted by steam can be used to reduce component holdup in some cases; however, column life may be seriously shortened. Passing the carrier gas through a pre-column containing copper sulfate ($CuSO_4 \cdot 5H_2O$) for wetting may have a lesser effect on substrate stripping (1).

6. Apparatus

6.1 *Gas System:*

6.1.1 *Gas Regulators*—High quality pressure regulators should be used to ensure a steady flow of gas to the instrument. If temperature programming is used, differential flow controllers should be installed in the carrier gas line to prevent a decrease in flow as the pressure drop across the column increases due to the increasing temperature. An unsteady flow will create an unstable baseline.

6.1.2 *Gas Transport Tubing*—New tubing should be washed with a detergent solution, rinsed with cold water, and solvent rinsed to remove residual organic preservatives or lubricants. Ether is an effective solvent. The tubing is then dried by flushing with nitrogen.

6.1.3 *Gas Leaks*—The gas system should be pressure checked daily for leaks. To check for leaks, shut off the detector and pressurize the gas system to approximately 103 kPa (15 psi) above the normal operating pressure. Then shut off the tank valve and observe the level of the pressure gauge. If the preset pressure holds for 10 min, the system can be considered leak-free. If the pressure drops, a leak is indicated and should be located and eliminated before proceeding further. A soap solution may be

used for determining the source of leaks, but care must be exercised to avoid getting the solution inside the tubing or instrument since it will cause a long lasting, serious source of interference. Leaks may also occur between the instrument gas inlet valve and flame tip. This may be checked by removing the flame tip, replacing it with a closed fitting and rechecking for pressure stability as previously noted.

6.1.4 *Gas Flow*—The gas flow can be determined with a bubble flow meter. A micro-rotameter in the gas inlet line is also helpful. It should be recalibrated after each readjustment of the gas operating pressure.

6.2 *Injection Port*—The injection port usually is insulated from the chromatographic oven and equipped with a separate heater that will maintain a constant temperature. The temperature of the injection port should be adjusted to approximately 50 C above the highest boiling sample component. This will help minimize the elution time, as well as reduce peak tailing. Should thermal decomposition of components be a problem, the injection port temperature should be reduced appropriately. Cleanliness of the injection port in some cases can be maintained at a tolerable level by periodically raising the temperature 25 C above the normal operating level. Use of disposable glass inserts or periodic cleaning with chromic acid can be practiced with some designs. When using samples larger than 5 μl, blowback into the carrier gas supply should be prevented through use of a preheated capillary or other special design. When using 3.175-mm (0.125-in.) columns, samples larger than 5 μl may extinguish the flame depending on column length, carrier gas flow, and injection temperature.

6.2.1 *Septum*—Organics eluting from the septum in the injection port have been found to be a source of an unsteady baseline when operating at high sensitivity. Septa should be preconditioned. Insertion of a new septum in the injection port at the end of the day for heating overnight will usually eliminate these residuals. A separate oven operating at a temperature similar to that of the injection port can also be used to process the septa. The septa should be changed at least once a day to minimize gas leaks and sample blowback. Septa with TFE-fluorocarbon backings minimize organic bleeding and can be used safely for longer periods.

6.2.2 *On-Column Injection*—While injection into the heated chamber for flash vaporization is the most common injection set-up, some analyses (for example, organic acids) are better performed with on-column injection to reduce ghosting and peak tailing and to prevent decomposition of thermally degradable compounds. This capability should be built into the injection system. When using on-column injection a shorter column life may occur due to solid build up in the injection end of the column.

6.3 *Column Oven*—The column ovens usually are insulated separately from the injection port and the detector. The oven should be equipped with a proportional heat and a squirrel-cage blower to assure maximum temperature reproducibility and uniformity throughout the oven. Reproducibility of oven temperature should be within 0.5 C.

6.3.1 *Temperature Programming*—Temperature programming is desirable when the analysis involves the resolution of organics with widely varying boiling points. The column oven should be equipped with temperature programming between 50 and 350 C with selectability of several programming rates between 1 and 60 deg/min provided. The actual column temperature will lag somewhat behind the oven temperature at the faster programming rates. Baseline drift will often occur because of increased higher temperatures experienced during temperature programming. This depends on the stability of the substrate and operating temperature range. Temperatures that approach the maximum limit of the liquid phase limit the operating range. Utilization of dual matching columns and a differential electrometer can minimize the effect of drift; however, the drift is reproducible and does not interfere with the analysis in most cases.

6.4 *Detector*—The combination of high sensitivity and a wide linear range makes the flame ionization detector (FID) the usual choice in trace aqueous analysis. The flame ionization detector is relatively insensitive to water vapor and to moderate temperature changes if other operating parameters remain unchanged. If temperature programming is used, the detector should be isolated from the

oven and heated separately to ensure uniform detector temperature. The detector temperature should be set near the upper limit of the programmed temperature to prevent condensation. The detector should also be shielded from air currents which could affect the burning characteristics of the flame. Sporadic spiking in the baseline indicates detector contamination; cleaning, preferably with diluted hydrochloric acid (HCl, 5 + 95), and an ultrasonic wash with water is necessary. Chromic acid also can be used if extreme care is taken to keep exposure times short and if followed by thorough rinsing. Baseline noise may also be caused by dirty or corroded electrical contacts at switches due to high impedance feedback.

6.5 *Recorder*—A 1-mV, 1-s, full-scale response, strip-chart recorder is recommended to obtain a permanent chromatogram. Chart speeds should be adjustable between 15 and 90 in./h.

6.6 *Power Supply*—A 105 to 125-V, a-c source of 60-Hz frequency suppling 20-A service is required as a main power supply for most gas chromatographic systems. If voltage fluctuations affect baseline stability, a voltage regulating transformer may be required in addition to the one incorporated within the chromatographic instrument.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all instances for gas purification, sample stabilization, and other applications. 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.[7] 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.

7.1.2 All chemicals used for internal standards shall be of highest known purity.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type I of ASTM Specifications D 1193, for Reagent Water.[6]

7.3 *Carrier Gas System*—Only gases of the highest purity obtainable should be used in a chromatographic system designated for trace-organic monitoring in water. The common carrier gases used with a flame ionization detector (FID) are helium and nitrogen. Trace contaminants in even the highest purity gases can often affect baseline stability and introduce noise. Absorption columns of molecular sieves (14 by 30-mesh) and anhydrous calcium sulfate ($CaSO_4$, 8 mesh) in series between the gas supply tank and the instrument will minimize the effect of trace impurities. These preconditioning columns, to remain effective, must be cleaned by back flushing them with a clean gas (nitrogen, helium) at approximately 200 C, or they must be replaced at regular intervals. Use of catalytic purifiers is also effective (4).

7.4 *Column:*

7.4.1 *Column Tubing*—For most organic analyses in aqueous systems, stainless steel is the most desirable column tubing material. However, when analyzing organics that are reactive with stainless steel, glass tubing should be used. With a flame ionization detector, maximum resolution with packed columns is achieved with long, small-diameter (3.175-mm (0.125-in.) and smaller) tubing. New tubing should be washed as described in 6.1.2.

7.4.2 *Solid Support*—Maximum column efficiency is obtained with an inert, small, uniform-size support. The lower limit of particle size will be determined by the allowable pressure drop across a column of given diameter and length. Elimination of fines will reduce the pressure drop and allow the use of smaller particles; the commonly used size is 80/100 mesh. Supports, which are not inert, may cause varying degrees of peak tailing. Few supports can be classified as totally inert; however, techniques are available to assist in the deactivation of the support. Chromosorb "W",[8] the least active type of diatomaceous-earth support, can be further deactivated by acid or base washing. A combination of acid washing and silanization (for example, dimethyldichlorosilane (DMCS), hexamethyldisilane)

[7] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N.Y., and the "United States Pharmacopeia."

[8] This material, while proprietary in nature, is distinctly superior to others which have been tried and is available from essentially all vendors of chromatographic supplies.

treatment may reduce the surface activity still further. However, silanization can decrease column life. DMCS treatment is particularly useful when low liquid loads are used. Treatment with specific chemicals that approximate the properties of the sample being analyzed has also proven successful. For example, terephthalic acid treatment of Carbowax 20M[8] reduces organic acid and phenolic tailing. Use of fluorocarbon supports can significantly reduce tailing. For low boiling materials, porous polymer beads formed by the polymerization of monomers such as styrene with divinyl benzene as a crosslinker are finding more application in trace analysis. Since there is no liquid phase, there is minimal column bleed during temperature programming. In addition, elimination of the conventional solid support removes the adsorptive sites which normally cause tailing. Caution must also be taken not to exceed the recommended maximum temperature limit of the fluorcarbon supports or of the porous polymer beads being used.

7.4.3 *Liquid Phases*—Maximum resolution and minimum baseline noise and drift are achieved with a relatively lightly loaded column (less than 5 percent) containing a stable substrate of low volatility. However, analysis of aqueous samples with light column loading produces shorter column life and a greater tendency for a shift in retention times and delayed elution as the column ages. Accelerated aging will occur if the maximum temperature limit of the liquid phase is exceeded or approached repeatedly. Substrates should be selected to permit operation at a temperature below the maximum allowable if at all possible. Selection of liquid phases should be based on the properties of the sample to be analyzed. In general, polar substrates will resolve polar compounds by order of relative volatility and polarity. Polar substrates will resolve nonpolar compounds by structural type. Nonpolar substrates will separate nonpolar compounds by volatility and polar compounds by structural type. For examples of applicable liquid phases for a particular application, consult published methods for specific organic classes.

7.4.4 *Column Conditioning*—All new columns should be pre-conditioned to drive off the residual contaminants which would foul the detector and cause severe baseline noise. New columns can be conditioned by attaching one end to the inlet port of the oven and allowing 20 to 30 ml/min of carrier gas to pass through the column either at 30 C above the expected maximum operating temperature or at the maximum temperature limit of the liquid phase, whichever is lower. The effluent end of the column should be vented. The column should not be attached to the detector during conditioning since eluting organics may foul the detector. Occasional 5-μl injections of water during the conditioning period will facilitate elution of the extraneous organics. The required conditioning period depends on the type of substrate and extraneous organics, but conditioning for about 12 h is adequate in most cases. A longer conditioning period may be necessary if peak tailing persists with polar compounds. The weight of column packing should be noted to allow preparation of identical replacement column, when needed.

7.5 *Detector Gases*—Hydrogen and air of the highest initial purity which have been further purified as described in 7.3, are fed to the detector. Hydrogen can also be used which is produced from the electrolytic decomposition of water.

7.6 *Glassware*—All glassware that will come into direct contact with the sample should be heated in an oven to 300 C (overnight if possible) as a final cleanup step. This will serve to remove any source of organic contamination from prior work.

8. Samples and Sampling Procedure

8.1 *Sample Collection*—Collect all samples in accordance with the applicable method of the American Society for Testing and Materials as follows:

D 510—Sampling Water,[6]
D 1192—Equipment for Sampling Water and Steam,[6] and
D 1496—Sampling Homogeneous Waste Water.[6]

Additionally sample containers and sample size and storage shall be as specified in 8.2 to 8.4.

8.2 *Sample Containers*—Care should be taken to collect a representative sample in a clean, completely full glass bottle. The screw cap should be lined with aluminum foil or TFE-fluorocarbon to reduce the sorption of

insoluble organics.

8.3 *Sample Size*—The sample size must be small to prevent overloading of the 3.175-mm (0.125-in.) columns generally used. For most aqueous analyses, a sample size of 2 to 5 μl is generally optimum. If the components of interest are of relatively high concentration, a 1-μl sample is to be used. At low concentrations, a sample approaching 10 μl can be used to increase the detectable limit although the measurement accuracy is slightly decreased since a 10-μl syringe is used. For the best accuracy, select a syringe with a capacity 50 percent greater then the size of the sample to be injected.

8.4 *Sample Storage*—Storage time of samples should be kept to a minimum. If storage cannot be avoided, the bacterial action should be minimized by refrigeration, by pH adjustment to about 2.0 (if organics are not acid degradable), or by the addition of 1 ml of saturated mercuric chloride ($HgCl_2$) solution to each liter of sample. Selection of a preservation procedure is dependent on the analysis being made.

9. Preparation of Chromatograph

9.1 *Column*—Select the appropriate column and install in the chromatographic oven. If the column is new, it should be preconditioned according to the directions in 7.4.4. The column should then be attached to the detector and the system checked for leaks according to 6.1.3. The column temperature requirements should be set according to the requirements outlined in the specific method being used.

9.2 *Gases*—With a flame ionization detector the gases require adjustment in the ratio of about 1 part carrier gas to 1 part hydrogen to 10 parts air. A typical flow for the carrier gas when using 3.175-mm (0.125-in.) tubing is 25 ml/min. Refer to the specific method being used for flow requirements.

9.3 *Electrometer and Recorder*—Adjust the electrometer and recorder as specified on the instrument instructions so that the pen is zeroed and the attenuation steps are linear. Based on the organic content of the sample to be analyzed, adjust the electrometer attenuation to give as near mid-scale deflections of the recorder pen as is practical.

9.4 *Baseline Stability*- Before proceeding with the analysis, check the stability of the recorder baseline with the pen at zero and the attenuation at the level to be used for the analysis. If sporadic peaks occur, further column conditioning may be necessary. The recorder, electrometer, flow controllers, and flame detectors should also be checked as a possible source of the sporadic peaks.

9.5 *Column Storage*—When columns are not in use, their ends should be capped. The need for reconditioning prior to their reuse at a later time will be indicated by making calibration runs with a known concentration of standards. Reconditioning is generally minimal if the column was adequately purged prior to storage.

10. Calibration and Standardization

10.1 *Qualitative:*

10.1.1 The basic method of tentative compound identification is by matching the retention times of known standards suspected to be present with retention times of unknown compounds under identical operating conditions. The absolute retention time is measured in minutes from the time of injection to the peak maximum. Since retention time may vary significantly with concentration of the particular organic compounds, identification is done more positively by spiking the sample with the suspected constituent and noting an increase in peak height. In some instances more than one compound may elute at the same time and therefore have identical retention times. This condition can often be recognized by a poorly shaped peak (that is, double apex or shoulder). When this occurs, additional column(s) with different physical and chemical properties will be required to separate the combined peaks. An alternative, which is frequently preferable, is to trap the peaks and identify them spectrometrically (see 11.7).

10.1.2 Relative retention times are developed by the insertion of a common noninterfering organic into each standard as well as into the unknown. The absolute retention time of the common organic is then divided into the absolute retention time of each organic being analyzed. Utilization of relative retention times improves qualitative accuracy by balancing out numerous chromatographic variations from run to run, for example, slight variations in column temperature, program-

ming rate, carrier gas flow, and sample size as well as column aging.

10.1.3 Based on the type and concentration of compounds expected in the sample to be tested, prepare similar standards in reagent water.

10.1.4 At least three relative retention times with a single column should be determined for each organic standard and the average used for qualitative analysis of the unknown sample. Relative retention times should be verified periodically.

10.1.5 One and two-column identifications are not usually sufficient for positive identification. A third column or spectrometric analysis of the trapped peak will be required for an unequivocal identification.

10.2 *Quantitative:*

10.2.1 The quantitative measurement of each component is determined from the area under the individual chromatographic peaks. Peak areas can be determined more efficiently by mechanical or electronic integrators. If the peaks are symmetrical and sharp with minimum tailing, peak height can be used for estimating quantitative response for expediency in routine monitoring type analysis. The height is measured from the peak maximum to the baseline. If the peak occurs in an area of baseline drift, approximate the actual base of the peak for measuring purposes. Measuring the peak width at one half the peak height and multiplying it by the peak height will approximate the peak area. The error increases as the peak width becomes smaller or as peak tailing increases.

10.2.2 Insertion of an internal standard is useful for quantitative analysis. When response is calculated relative to an internal standard, compensation is provided for the inadvertent changes in chromatographic conditions. Selection of the internal standard should be based on its separation from other peaks, stability, and if possible on mid-chromatogram elution and structural similarity to the components being analyzed. The internal standard should be applied at approximately the expected average concentration of the organic constituents. When temperature programming is used, two internal standards may be needed, one for low-boiling and one for high-boiling constituents.

10.2.3 Mass response ratios are determined by the injection of standards containing the same concentration of both the internal standard and the individual components suspected to be in the samples to be tested. For accurate quantitative work triplicate injections should be made on a conditioned column with the average being used for further calculations. All chemicals used should be of the highest known purity, so that the appropriate correction may be made when calculating the final response factors. Response factors should be rechecked periodically.

10.2.4 The linearity of the response factors should be verified by varying the concentration of the individual components over the concentration range of interest while holding the internal standard concentration constant. These ratios when plotted against concentration should yield a straight line that passes through zero. Chromatographic operating conditions should always be recorded on the graph. Attenuation should preferably be adjusted to keep the peaks at approximately 50 percent of full scale, if possible. The final peak areas or heights are adjusted according to the electrometer attentuation setting used for calibration.

11. Sample Testing Procedure

11.1 *Injection Practice*—Use a firm, relatively fast injection technique so that the sample can be injected either into the middle of the injection port for flash vaporization, or approximately 2 in. down the column for on-column injection in a slug-like condition. Slow injections may cause poor resolution and spreading. Use the same rhythm each time. Wash the syringe several times between injections with acetone, then rinse with water, and air dry by attaching to a vacuum line. Flush the syringe at least two times with the sample to be analyzed. Remove the bubbles by pumping the syringe plunger followed by a slow drawup of the sample. When injecting large samples at high inlet pressure (for example, 50 psi), hold the plunger so as to prevent its blowout caused by the pressure buildup in the injection port; special syringes are needed for high-pressure work.

11.1.1 *Sample Injection*—Use direct aqueous injection whenever possible to pre-

vent both the loss of some components and the introduction of extraneous peaks that may result from concentration techniques. However, when analyses are in the part per billion range, concentration techniques will be required. Carbon adsorption, gas stripping, solvent extraction, and freezeout have been shown to increase component concentration to detectable levels (1,5,6).

11.2 Establish operating conditions identical to those used for calibration and standardization. If changes are required because of sample peculiarities, repeat calibration and standardization using the new conditions. If an internal standard is used, minor changes in operating conditions are tolerable.

11.3 Inject sample prior to insertion of internal standard to assist in either the selection of the internal standard, or to assure that the internal standard selection is well resolved from component peaks in the sample. An open position in the chromatogram is selected for this purpose.

11.4 Add the internal standard(s) into the sample at a concentration approximating the components to be analyzed and repeat the analysis.

11.5 Refer to the specific method for suggested sample size; 3 to 5 µl are often used.

11.6 Determine the absolute retention times of the individual components in the sample. Calculate relative retention times using the retention time of the internal standard in the denominator. Refer to the previously developed listing for relative retention times of known compounds on specific columns; if absolute retention times are used, run standards several times during the test series. Repeat on additional columns as necessary to increase qualitative accuracy.

11.7 Trap individual peaks for confirmatory analysis. Mass spectrometric analysis of trapped components is often most informative; however, infrared spectrographic analysis, thin-layer chromatography, and microcoulometry or other specialized detectors (for example, flame photometric detector, modified flame halogen detector) are also useful.

11.8 Adjust attenuation to keep all peaks on scale and preferably near 50 percent of full scale. After component identifications have been completed, triplicate determinations should be made at identical instrument conditions for quantitative analysis. Water washes are usually injected between samples to eliminate ghosting.

11.9 Measure peak areas or height (symmetrical, non-tailing peaks required) and average the results.

12. Calculation

12.1 Tentative identification of individual components is based primarily on relative retention times. Report confirmative identifications based on additional columns and on spectrometric analysis of trapped fractions.

12.2 Use the following formula to convert peak area to concentration in milligrams per liter:

$$\text{Concentration of } EC, \text{ mg/liter} = \frac{\text{peak area } EC}{\text{peak area } IS} \times \frac{\text{concentration } IS \text{ (mg/liter)}}{\text{mass response ratio}}$$

where:

EC = eluted component, and

IS = internal standard

Previously determine mass response ratio by dividing the response of the eluted component by the response of the internal standard at the same concentration.

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REFERENCE NO. 4

NITRILES IN AQUEOUS SOLUTION BY GAS-LIQUID CHROMATOGRAPHY

Designation: D 3371 – 74 T

Tentative Method of Test for NITRILES IN AQUEOUS SOLUTION BY GAS-LIQUID CHROMATOGRAPHY[1]

This Tentative Method has been approved by the sponsoring committee and accepted by the Society in accordance with established procedures, for use pending adoption as standard. Suggestions for revisions should be addressed to the Society at 1916 Race St., Philadelphia, Pa. 19103.

1. Scope

1.1 This method covers nitriles that can be separated and detected quantitatively at a limit of approximately 1 mg/litre by aqueous injection on a selected gas-liquid chromatographic column.

1.2 This method utilizes the procedures and precautions as described in Recommended Practice D 2908.

2. Applicable Documents

2.1 *ASTM Standards:*

D 2908 Recommended Practice for Measuring Volatile Organic Matter in Water by Aqueous Injection Gas Chromatography[2]

3. Significance

3.1 Nitriles at concentrations of a few milligrams per litre are potentially toxic to aquatic life. Nitriles in waste water discharges should be detected and controlled.

3.2 Gas-liquid chromatography (GLC) can detect and determine mixtures of nitriles at levels where wet chemical procedures are not applicable.

4. Special Comments

4.1 It is recommended that samples that cannot be analyzed immediately, be quick frozen for preservation. Samples should be neutralized to pH 7 at the time of collection to minimize hydrolysis of the nitrile groups.

4.2 Samples of nitriles to be employed as standards should be considered to be unstable. Storage in a freezer is recommended.

4.3 It is not always practical to translate operating conditions directly from one GLC instrument to another. An operator should optimize his instrument to a particular procedure, for example, injection and detection temperature, flow rates, etc.

5. Typical Chromatograms

5.1 The following instrument parameters were used to obtain the typical chromatograms (See Figs. 1 and 2).

5.1.1 *Column*—⅛ in. outside diameter stainless steel, 8 ft long packed with a porous styrene divinylbenzene polymer.

NOTE—"Chromosorb" 101, 50/60 mesh, was used for the typical chromatograms.

5.1.2 *Detector*, flame ionization.

5.1.3 *Temperatures:*

Injection port	240°C
Detector	240°C
Oven, isothermal	130°C
Oven, programmed at 10°C/min	110°C to max of 200°C

5.1.4 *Carrier Gas*, helium at 25 ml/min.

5.1.5 *Sample Size:*

isothermal 5 μl
programmed 3 μl

5.1.6 *Recorder*, ¾ in./min chart speed and 1 mV full-scale response.

5.2 *Kovats Index Values:*[3]

Compounds	Relative Retention	Kovats Index
Acetonitrile	1.00	470
Acrylonitrile	1.25	512

[1] This method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D 19.05 on Inorganic Constituents in Water.

Current edition approved Nov. 4, 1974. Published February 1975.

[2] *Annual Book of ASTM Standards*, Part 31.

[3] *Gas Chromatographic Data Compilation, ASTM A.M.D 25A*, Am. Soc. Testing Mats., 1967.

Propionitrile	1.67	570
Methoxy acetonitrile	2.21	635[a]
Butyronitrile	2.50	678
Isovaleronitrile	3.04	740[a]
Valeronitrile	3.38	783
Hexanenitrile	4.25	905[a]
Benzonitrile	5.42	990

6. Precision

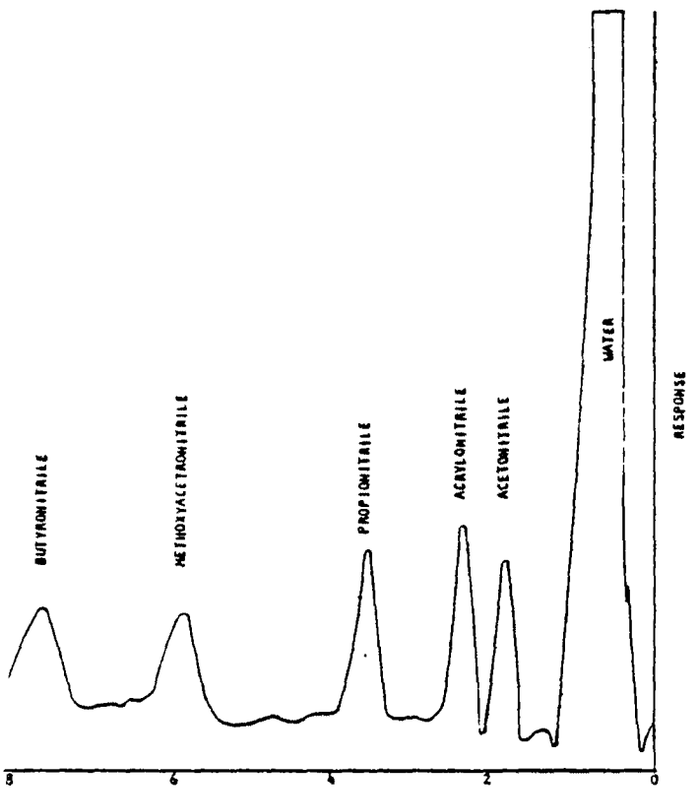
6.1 The precision of this method within the range from 10 to 60 mg/litre of standards in distilled water may be expressed as follows:

Compound	S_T
Acetonitrile	$S_T = 0.015$ (mg/litre) + 0.9
Propionitrile	$S_T = 0.088$ (mg/litre) − 0.6
Methoxy Acetonitrile	$S_T = 0.097$ (mg/litre) − 0.1
Butyronitrile	$S_T = 0.10$ (mg/litre) − 0.4

where:

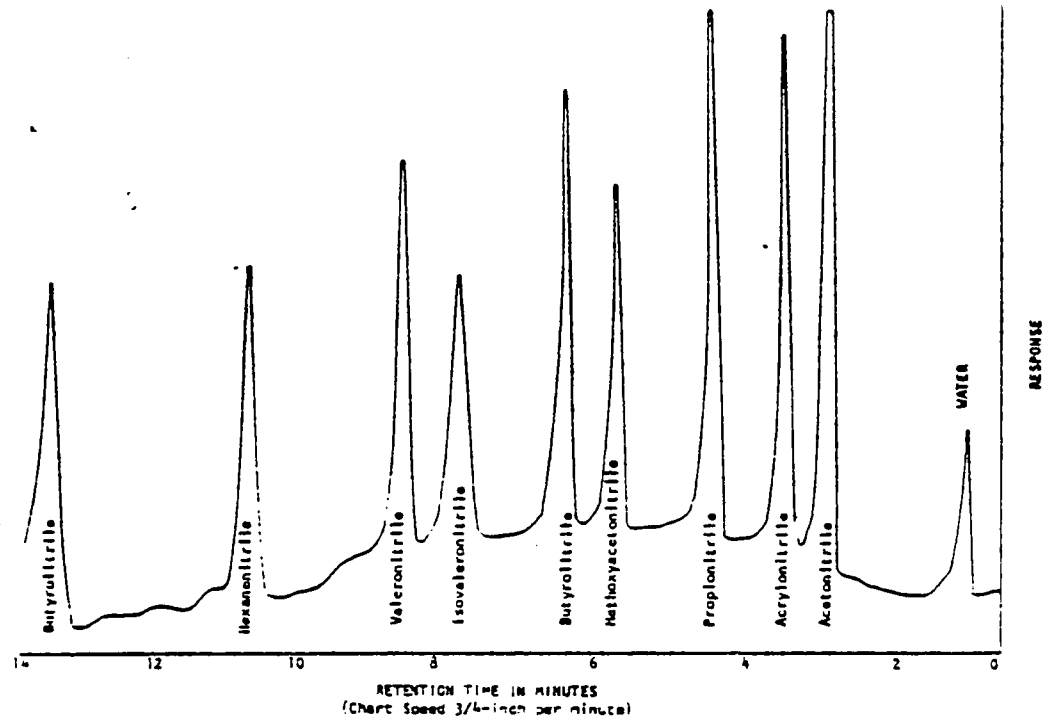
S_T = overall precision, and
mg/litre = concentration of the specific compound

[a] Kovats index values estimated from relative retention data because standard compound was not readily available.



Column Packing - Chromosorb 101, 50/60 mesh
Carrier Gas - Helium at 25 ml/min
Temperature - Isothermal operation of the column at 130°C
Sample Size - 5 microliters containing 10 mg/l of each nitrile

FIG. 1—Isothermal Chromatographic Analysis of Nitriles in Aqueous Solution



Column Packing - Chromosorb 101, 50/60 mesh
Carrier Gas - Helium at 25 ml/min
Temperature - Programmed operation at 10°C/min from 110°C to a maximum of 200°C
Sample Size - 3 microliters containing 1,500 mg/l of each nitrile

FIG. 2—Proposed Temperature Chromatographic Analysis of Nitriles in Aqueous Solution

REFERENCE NO. 5

DIRECT ANALYSIS OF WATER SAMPLES FOR ORGANIC POLLUTANTS WITH GAS-CHROMATOGRAPHY--MASS SPECTROMETRY

Direct Analysis of Water Samples for Organic Pollutants with Gas Chromatography–Mass Spectrometry

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A direct aqueous injection gas chromatography–mass spectrometry (GC/MS) procedure was explored as a supplement to conventional solvent extraction for analysis of the organic pollutants in water and wastewater samples. Studies were made of the effects of relatively large pressures of water vapor on the well established electron impact fragmentation patterns, quadrupole GC/MS system performance, interactive background subtraction, and detection limits. It was concluded that direct aqueous analysis is a valuable supplemental procedure for the detection of volatile compounds that are not found with solvent extraction.

Effective water pollution control requires analytical methodology that is capable of generating correct identifications and measurements of the concentration of the organic pollutants in water samples. This methodology is necessary to determine the exact sources of pollution, to set effluent standards for toxic pollutants, to enforce effluent guidelines, to evaluate the effectiveness of treatment facilities, and to determine the causes of taste, odor, and fish kills.

In the past, a very significant amount of research, frequently over several weeks or months, was required to obtain identifications of the trace organics in water samples. Often this effort resulted in just a few identifications and it occasionally produced erroneous results. The development of computerized gas chromatography–mass spectrometry (GC/MS) revolutionized the field of trace organic analysis (*1*, *2*). Today many laboratories have the capability to make more than a dozen unambiguous identifications with just a few man-hours of effort.

The first sample work-up methods used with GC/MS in organic water pollutant analysis were minor modifications of standard solvent extraction procedures which were developed for pesticide analyses. These procedures together with GC/MS are very effective in isolating, concentrating, and identifying extractable and volatile organic pollutants at levels as low as 10 parts per trillion (10 ng/l). This great sensitivity is achieved, in part, by an efficient concentration of a relatively large volume of organic solvent extract to a very small volume. Concentrations of trace organics by a factor of 10^3 is not uncommon.

Solvent extractions does, however, possess several limitations including the loss of very volatile organic pollutants (*e.g.*, chlorinated solvents) by vaporization during the extract concentration step. Another difficulty is the failure to extract efficiently a variety of volatile but water soluble organic pollutants (*e.g.*, low molecular weight alcohols and ketone solvents). A supplemental work-up procedure for the analysis of these compounds is required. Perhaps the simplest and most direct approach is the analysis of the unaltered water samples by GC/MS.

The gas chromatography of unaltered water samples is feasible and has been known for some time (*3–7*). It has been practiced only sparingly, however, because conventional GC detectors (*e.g.*, the flame ionization detector) do not produce sufficient information to unequivocally distinguish among the enormous variety of different organic compounds that could be present in a water sample. Computerized GC/MS overcomes this difficulty since the mass spectrometric data are frequently sufficient for an unambiguous characterization of most of the very volatile compounds present.

Routine direct aqueous GC/MS analysis for organic water pollutants offers the potentially very significant additional benefit of *instant analysis*. Since no time and labor consuming pre-analysis treatment is required, a relatively large number of samples may be processed per unit of time at a relatively low unit cost.

A study was made of the applicability of this technique to water pollutant identification.

Difficulties that might be anticipated with water as a solvent for GC/MS analysis were studied also. Since the solvent extract concentration step was eliminated, sensitivity limitations were defined. Traditionally water is considered highly detrimental in magnetic deflection mass spectrometers. It may facilitate discharges from 2–8 kV accelerating potentials and cause degradation of Cu–Be electron multiplier detectors. However the effects of large quantities (1–10 μl) of water injected into the GC/MS on the performance of the quadrupole mass spectrometer and the sample enrichment device were unknown. Also unknown was the effect of large quantities of water vapor on the well established electron impact fragmentation patterns of organic compounds.

The approach used was to analyze representative waste samples and well-defined mixtures of compounds to ascertain the effect of water on the system and fragmentation patterns. The levels of detection of a variety of classes of compounds were determined with several new and old GC column packing materials.

EXPERIMENTAL

Instrumentation. The water samples were analyzed using direct on-column injection into a Varian Model 1400 gas chromatograph interfaced with a Finnigan Model 1015 C quadrupole mass spectrometer system controlled by a Systems Industries 150 data acquisition and control system (*2*). The MS was the only detector used. The data were displayed as plots on a cathode ray tube dis-

[1] To whom correspondence should be addressed.

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Table I. Selected Organic Compounds Analyzed by GC/MS

Compound	Quantity injected, ng	Quantity solvent, μL	Solvent	Concentration, mg/L	GC column	GC column conditions
Blank		1	Water	...	1	*a*
n-Decane	100	1	Acetone	100	1	*b*
n-Decane	100	1	Water	100	1	*b*
MIBK	100	1	Acetone	100	1	*b*
MIBK	100	1	Water	100	1	*b*
n-Butyl acetate	100	1	Acetone	100	1	*b*
n-Butyl acetate	100	1	Water	100	1	*b*
n-Amyl alcohol	100	1	Acetone	100	1	*b*
n-Amyl alcohol	100	1	Water	100	1	*b*
p-Cresol	100	1	Acetone	100	1	*c*
p-Cresol	100	1	Water	100	1	*c*
Acetophenone	100	1	Acetone	100	1	*c*
Acetophenone	100	1	Water	100	1	*c*
2-Phenylethanol	100	1	Acetone	100	1	*c*
2-Phenylethanol	100	1	Water	100	1	*c*
n-Hexadecane	100	1	Acetone	100	1	*c*
n-Hexadecane	100	1	Water	100	1	*c*
sec-Butyl alcohol	100	1	Water	100	1	*d*
Acetone	100	1	Water	100	1	*d*
Methyl-*n*-octanoate	100	1	Water	100	1	*d*
Chloroform	100	1	Water	100	1	*a*
DME	20	2	Water	10	1	*a*
n-Amyl alcohol	5	1	Water	5	1	*a*
n-Amyl alcohol	10	10	Water	1	1	*a*
Methylene chloride	10	10	Water	1	1	*a*
Methylene chloride	5	1	Water	5	1	*a*
Ethyl acetate	50	1	Water	50	2	*e*
DME	50	1	Water	50	2	*e*
MIBK	50	1	Water	50	2	*e*
Dioxane	50	1	Water	50	2	*e*
Acetophenone	50	1	Water	50	2	*e*
o-Chlorophenol	50	1	Water	50	2	*e*
m-Cresol	50	1	Water	50	2	*e*

[a] 100° isothermal; [b] 70° for 2 min, then 6°/min to 120°; [c] 150° for 2 min; then 6°/min to 180°; [d] 100° for 1 min, then 6°/min to 150°; [e] 60° for 3.5 min, then 12°/min to 180°.

play unit (Tektronix Model 4010) or a flat-bed plotter (Houston Instruments Model DP-1). The GC/MS interface utilized an all glass jet-type enrichment device to deliver the sample directly into the ion source of the MS. The batch inlet system was all glass with a constant-leak opening that introduced the sample directly into the ion source of the MS. The batch inlet was heated to 100° for the analyses. Other conditions that were held constant throughout the analyses were: helium carrier gas at a flow rate of about 30 ml/min; temperature of the GC injection port at 190°; the temperatures of the interface and transfer line at 210°; detector manifold temperature at 100°; pressure in MS of 10^{-5} Torr; ionizing voltage of 70 eV; a filament current of 500 μA; electron multiplier at 3000 volts; mass range scanned from 20–200 amu at an integration time of 10 msec/amu; and sensitivity at 10^{-7} A/volt unless otherwise specified. The quadrupole MS operating parameters were adjusted to give the normal ion abundances for a standard reference compound (*8*).

Gas Chromatography Columns. *Column 1.* A 12-foot coiled stainless steel (o.d. 0.125 in.) tube was packed with 60/80 mesh Gas Chrom Q coated with 5% Carbowax 20 M.

Column 2. A 7-foot coiled glass column (i.d. 2 mm) was packed with 60/80 mesh acid-washed Chromosorb W coated with 10% Free Fatty Acid Phase (FFAP).

Column 3. An 8-foot coiled glass column (i.d. 2 mm) was packed with 50/60 mesh Chromosorb 101. Special care was taken to flush the column sufficiently with helium (40–50 min) to remove any residual air from the packing before heating.

Method 1. An organic compound (1 μl) was vaporized into the batch inlet reservoir and allowed to leak slowly through a glass frit directly into the ion source of the mass spectrometer. The mass spectrum of the compound was acquired repetitively from 20 to 200 amu using computer control, and the data were stored on a disk storage device. As the MS data were being generated and stored, 1 μl of tap water was injected onto GC Column 1 at 100°. After the water eluted from the column into the detector and was pumped out of the MS, valves were opened and the organic compound was pumped from the batch inlet. The experiment was terminated, and the data were recalled for evaluation of the mass spectra. The organic compounds that were analyzed using this method include the following: 1,2-dimethoxyethane (DME), di-*n*-butyl amine, *sec*-butyl alcohol, methyl-*n*-octanoate, acetic acid, *n*-hexadecane, *n*-amyl alcohol, and *n*-butyl acetate.

Method 2. Water (1 μl) was vaporized into the batch inlet reservoir and allowed to leak continuously into the detector. Then 1 μl of acetone containing 100 ng each of *n*-decane, methyl-isobutyl ketone (MIBK), *n*-butyl acetate, and *n*-amyl alcohol was injected onto Column 1 at 70°. After the acetone solvent was pumped out of the detector, the ionizer was turned on and the mass spectra of the organic compounds were repetitively scanned while water was continuously leaking into the ion source. The GC temperature was programmed from 70 to 120° at 6°/min.

Method 3. The mass spectra of selected organic compounds were measured by injecting aqueous and/or acetone solutions into the GC/MS. The compounds studied, quantities, solvents, and GC conditions are shown in Table I.

Waste Effluent Sample. This sample was acquired from the effluent of a lagoon type chemical treatment facility and was analyzed by direct injection of 1 μl onto Column 3. The column tem-

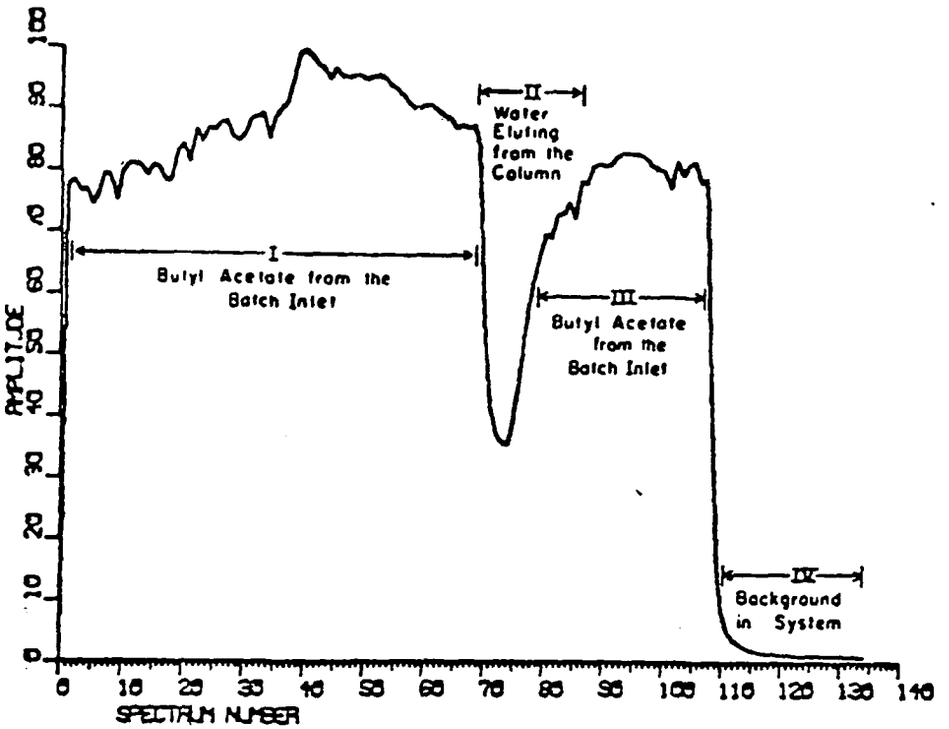

Figure 1. An ion abundance chromatogram obtained from water eluting from Column 1 while *n*-butyl acetate was permitted to leak continuously into the ion source from the batch inlet

perature was held at 120° for 3 min, then programmed to 180° at 12°/min.

Tap Water Sample. A 5-μl sample of tap water was injected onto Column 3 at 140°. Ions of mass 47, 83, and 85 were repetitively observed with an integration time of 450, 900, or 1350 msec which was determined dynamically to maximize signal to noise. The technique of subset data acquisition was described previously (2). The technique of integration time as a function of signal strength will be described in the near future (8). Additional details on the analysis of chloroform in tap water will be presented in a future paper (9).

RESULTS AND DISCUSSION

The mass spectra of a number of organic compounds were recorded while water was present in relatively high proportion in the ion source. The purpose of these experiments was to determine the effects of water on well known fragmentation patterns. Method 1 was used to study the effect of an increase in water pressure from the GC inlet (Column 1) on the fragmentation patterns of several compounds which were permitted to leak continuously from the batch inlet. For example, mass spectra of *n*-butyl acetate were acquired and recorded continuously during one experiment and Figure 1 shows the ion abundance chromatogram that was obtained. In regions I, II, and III, *n*-butyl acetate spectra were acquired. In region II, water eluted from the column and subsequently was pumped out of the mass spectrometer. In region IV, the batch inlet system valve was closed and *n*-butyl acetate was pumped from the mass spectrometer. From this experiment, mass spectra of *n*-butyl acetate were plotted before (spectrum 60), during (spectrum 75), and after (spectrum 85) water eluted from the GC inlet system. Spectrum 130 was subtracted from each spectrum to correct for background ions. The masses and abundance data from these spectra are shown in Table II. For any given ion, the relative abundance is nearly identical in all three spectra, which indicated that water had no significant effect on the fragmentation processes of this compound.

Table II. Mass Spectra of Butyl Acetate from Batch Inlet with Water Eluting from GC

	Relative ion abundances		
m/e	Spectrum No. 60–130	Spectrum No. 75–130	Spectrum No. 85–130
39	5	5	6
40	1	0	1
41	17	19	19
42	5	4	6
43	100	100	100
44	3	4	3
45	2	2	2
55	7	7	7
56	35	32	36
57	8	8	9
58	2	2	2
61	12	12	13
71	2	2	2
73	12	12	14
87	2	2	2

Similar results were obtained with the other compounds studied by Method 1. These compounds included methyl *n*-octanoate which has a base peak in its mass spectrum that is due to a McLafferty rearrangement. In this well known process, a gamma hydrogen is transferred to the carbonyl oxygen and a neutral C_6H_{12} fragment is expelled from the molecular ion. It was clear that the relatively high pressure of water present during the ionization did not cause ion-molecule reactions or other effects that would alter this fragmentation process. We concluded that the ion source design, pumping speeds, etc. that were employed were such that disruptive effects were precluded in general.

This conclusion was confirmed by several experiments which used Method 2 to study the effect of a constant water pressure from the batch inlet on the fragmentation pattern of several compounds introduced from the GC inlet (Column 1). Again water vapor was present in the ion source in relatively large quantities at precisely the same

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(9) T. A. Bellar and J. J. Lichtenberg, *Environ. Sci. Technol.*, in press.

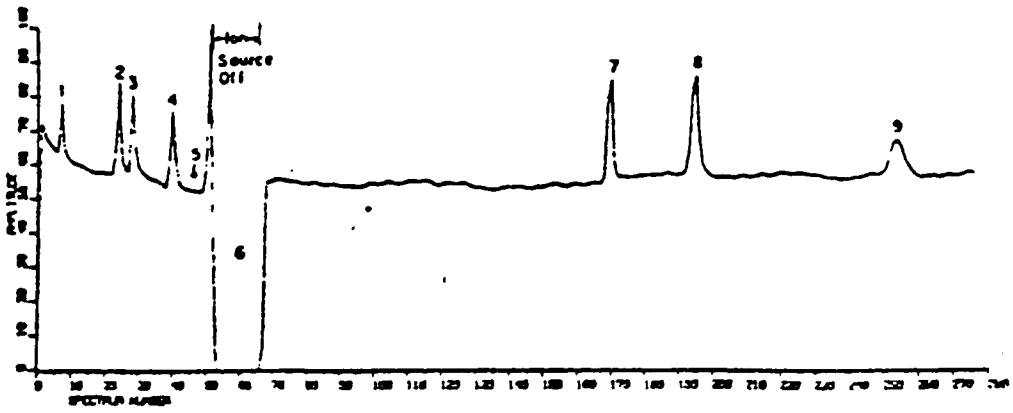

Figure 2. An ion abundance chromatogram obtained from a mixture of 50 ng of each of the following compounds in tap water on Column 2

(1) carbon dioxide from the tap water solvent; (2) ethyl acetate; (3) 1,2-dimethoxyethane; (4) methyl isobutyl ketone; (5) dioxane; (6) water; (7) acetophenone; (8) *o*-chlorophenol; and (9) *m*-cresol

time the compounds were undergoing ionization and fragmentation. One of the compounds studied was *n*-amyl alcohol which undergoes an electron impact induced dehydration reaction. In this and all other experiments the presence of water in the MS detector system caused no noticeable effect on the observed mass spectra.

A number of additional experiments (Method 3) were conducted to support these conclusions. The compounds shown in Table I were introduced into the mass spectrometer through the GC inlet. The compounds were selected as representatives of several classes of compounds commonly found as volatiles in water samples. The mass spectra that were obtained from acetone and water solutions were compared and found to be identical in all cases.

Precautions and System Performance. In principle, the sample enrichment device in the GC/MS interface should reduce the amount of water which enters the ion source of the mass spectrometer. Although no quantitative measurements were made, our qualitative observations support this expectation. As much as 10 μl of water was introduced onto the GC column in a single injection and a number of 1- to 10-μl injections were made during a work day with no apparent detrimental effects on system performance or sensitivity.

With cross-linked porous polymer packed columns, *e.g.*, column 3, from which water elutes very quickly, the ion source potentials (5–100 V) and electron multiplier voltage (3 kV) were not applied and data acquisition was not begun until water eluted. This is also standard procedure for organic solvent extracts. With other columns, *e.g.*, Columns 1 and 2, from which water elutes much later and after some organics, the source and multiplier potentials were applied immediately after injection and left on during solvent elution with small, *i.e.*, 1 μl, water injections. With larger quantities, these potentials were usually removed during elution of the water (Figure 2). A downward drift in the ionizing current was observed with the ion source on while 1 μl or more of water eluted (Figure 1).

During the course of these experiments over more than 18 months, frequent observations were made of overall system performance. The performance measurement was the ability of the system to produce, from a 20-ng injection, the *correct* electron impact fragmentation pattern of a reference compound (8) with a molecular weight of 442. The background noise was never observed at greater than 2–3% of the base peak. Normal degradation in the performance of a quadrupole mass spectrometer is revealed by a loss in sensitivity (signal/noise) and resolution at masses greater than ~250 amu. This is caused frequently by an accumulation of carbon and other extraneous deposits on the ion source and quadrupole rods. Surprisingly, it was our qualitative observation that normal performance degradation was retarded somewhat during the period of intensive study of aqueous injections. We tentatively credit this apparent effect to a *steam cleaning* phenomena.

Background Subtraction. Care must be taken during computer assisted background subtraction if the well established fragmentation patterns are to be observed. For example, *n*-decane was chromatographed in acetone and water on Column 1 (Table I). The base peak of *n*-decane, after background subtraction, in acetone was mass 57 and, in water, mass 43. The background spectrum selected for subtraction in each case was immediately in front of the *n*-decane peak. Acetone has a base peak of mass 43 and residual acetone in the spectrometer contributed a large mass 43 ion to the background spectrum. Therefore, the mass 43 ion abundance was reduced substantially by background subtraction in the spectrum of *n*-decane in acetone, and mass 57 became the base peak. This did not occur in water and is a clear advantage of a non-organic solvent for GC/MS analyses of organic pollutants.

However, an ion of mass 44 was observed as the base peak for a tap water blank on Column 1 (data acquisition began at mass 20). This was not caused by dissolved carbon dioxide, which generally elutes as a sharp peak (Figure 2). It may emanate from the continuous decomposition of carbonates or other dissolved compounds. *n*-Butyl acetate in water eluted from Column 1 on the leading edge of the water peak. Subtraction of a background spectrum from before the *n*-butyl acetate peak gave a spectrum similar to that of *n*-butyl acetate but with mass 44 as the base peak. If a spectrum for subtraction was chosen from near the apex of the water peak, the mass 44 was eliminated and the correct *n*-butyl acetate spectrum was obtained. This illustrates one necessary precaution of aqueous injection GC/MS. The ability to rapidly (10–15 sec) view a mass spectrum histogram on a CRT display greatly facilitates background subtraction and other types of real time interactive data reduction.

Column Selection. The selection of a GC column for aqueous GC/MS analysis depends on the types of compounds sought in the analysis. If it is desired to search for low molecular weight volatile compounds, porous polymers (*e.g.*, Column 3) appear to be the best choice for a column packing material. If the aqueous analysis is to be extended into the types of compounds usually sought by solvent extraction, *e.g.*, phenol and substituted phenols, another column is required because elution times for higher molecular weight compounds become unacceptable. Either Carbowax (Column 1) or FFAP (Column 2) stationary phases are a reasonable choice. The disadvantages of these columns include the inability to observe, as distinct peaks, compounds

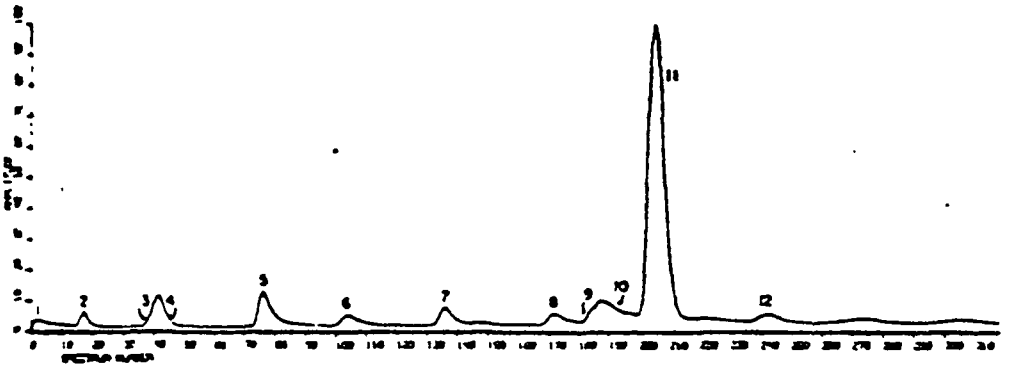

Figure 3. An ion abundance chromatogram obtained from a direct injection onto Column 3 of effluent from a lagoon chemical treatment facility.

The compounds identified were: (1) methanol; (2) ethanol; (3) acetone; (4) 2-propanol; (5) acetic acid; (6) 2-butanone; (7) propanoic acid; (8) 2-ethoxyethanol; (9) butanoic acid; (10) triethyl amine; (11) *N,N*-dimethylformamide, and (12) pentanoic acid

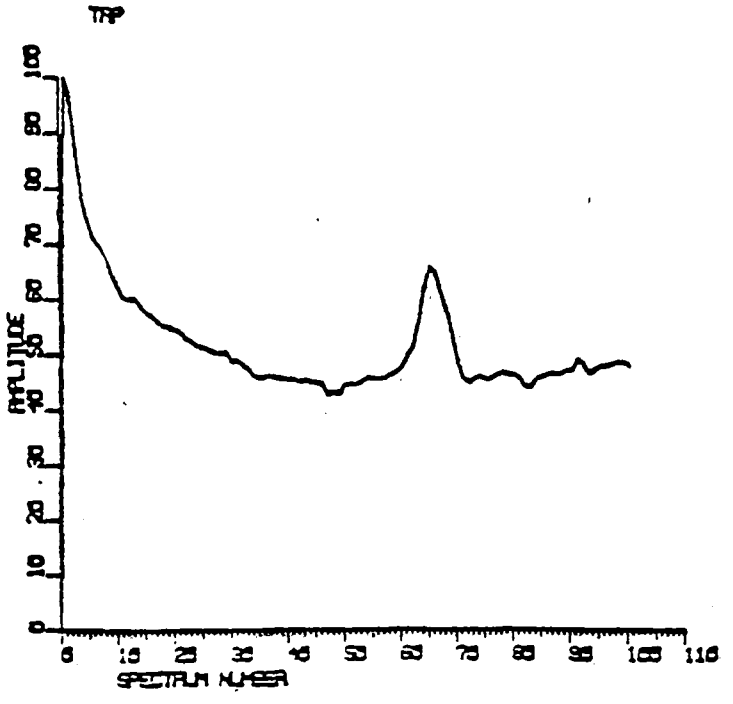

Figure 4. Ion abundance chromatogram obtained from tap water eluting from Column 3 with subset data acquisition at masses 47, 83, and 85

which have the same retention time as water. Also, as pointed out previously, it may be necessary to interrupt data acquisition during elution of water with these columns (Figure 2). None of the numerous specialty phases available for specific analyses were evaluated for this application.

Application to an Environmental Sample. Numerous water samples were collected from waste effluents, chemical spills, and waste treatment plants and submitted to aqueous injection GC/MS. The ion abundance chromatogram shown in Figure 3 was obtained from an aqueous injection of the effluent from a lagoon type chemical waste treatment plant. From each peak of the chromatogram, a mass spectrum was retrieved from the disk storage device. This provided an unequivocal identification of the pollutants still present in the effluent.

Detection Limits. The absolute detection limit of a quadrupole GC/MS system will vary widely and depend on a variety of factors including the efficiency of the GC column and enrichment device, the presence of carbon deposits on the ion source or rods, the adjustment of the ion source and rod potentials, the mass range scanned, the integration time per mass unit, the total scan time, and the signal-to-noise ratio required in any given mass spectrum. During the course of these experiments with the quadrupole GC/MS, it was possible to obtain a reasonably clean (signal/noise = 25 or greater) 40–400 amu mass spectrum in a 5-sec total scan time from about 5 ng of a volatile organic compound. A 5-μl aqueous solution containing a total of 5 ng of a compound has a concentration of 1 mg/l. (1 ppm) and this should be the approximate lower detection limit for a 40–400 amu 5-sec scan. Using a somewhat shorter mass range (20–200 amu), methylene chloride and *n*-amyl alcohol were mixed in water at the 1 mg/l. concentration and chromatographed using Column 1 (Table I). Acceptable mass spectra were obtained from this experiment. However, with the porous polymer packed column (Column 3), the detection level was about 10–20 mg/l. In general, the concentration required to obtain a reasonably clean MS was between 1–50 mg/l. This detection limit for conventional data acquisition is usually not sufficient for relatively clean water, *i.e.*, finished tap water or surface waters. However, it is more than adequate for the analysis of effluents and other relatively dirty water which frequently contains organic compounds at a concentration greater than 1 mg/l.

There are several methods available which may be used to extend the detection limit. Very large samples, *i.e.*, 50–100 μl may be injected if a solvent venting valve is installed and a column is used from which water elutes rapidly, *e.g.*, Column 3. Another approach to enhance sensitivity for specific compounds utilized data acquisition from subsets of the ions which are observed in conventional mass spectrometry (*2*). With this approach only a relatively few ions are monitored in real time with a relatively long integration time on each to substantially improve signal/noise by time averaging. Figure 4 shows a direct aqueous analysis of 5 μl of a finished tap water sample. Ions of mass 47, 83, and 85 were repetitively monitored with an integration time of 450–1350 msec which was determined dynamically as a function of signal strength. These ions were selected because they represent the three most abundant ions in the mass spectrum of chloroform. The peak observed had the retention time of chloroform which was estimated to be present in the 80–120 μg/l. concentration range.

CONCLUSION

Direct aqueous injection gas chromatography with a computer controlled quadrupole mass spectrometer detector is a powerful supplemental method for the unambiguous identification of the more volatile organic pollutants in water samples. Relatively large pressures of water vapor in the mass spectrometer have no significant effect on the

well established 70-eV electron impact fragmentation patterns of organic compounds or the performance of the quadrupole GC/MS system. The detection limits attained using conventional data acquisition were 1–50 ppm which makes the technique compatible with the concentrations of organic compounds found in domestic sewage and other waste effluent water samples. Greater sensitivity, to about 50 ppb, was attained with real time data acquisition from subsets of the ions used in conventional mass spectrometry. This technique made the method applicable to the analysis of relatively clean surface or drinking water.

ACKNOWLEDGMENT

We thank Tom Bellar of this Laboratory for the original suggestion to analyze tap water for chloroform.

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REFERENCE NO. 6

DETERMINATION OF ORGANOCHLORINE PESTICIDES IN INDUSTRIAL EFFLUENTS

1. METHOD FOR ORGANOCHLORINE PESTICIDES IN INDUSTRIAL EFFLUENTS

1. Scope and Application

1.1 This method covers the determination of various organochlorine pesticides, including some pesticidal degradation products and related compounds in industrial effluents. Such compounds are composed of carbon, hydrogen, and chlorine, but may also contain oxygen, sulfur, phosphorus, nitrogen or other halogens.

1.2 The following compounds may be determined individually by this method with a sensitivity of 1 µg/liter: BHC, lindane, heptachlor, aldrin, heptachlor epoxide, dieldrin, endrin, Captan, DDE, DDD, DDT, methoxychlor, endosulfan, dichloran, mirex, pentachloronitrobenzene and trifluralin. Under favorable circumstances, Strobane, toxaphene, chlordane (tech.) and others may also be determined. The usefulness of the method for other specific pesticides must be demonstrated by the analyst before any attempt is made to apply it to sample analysis.

1.3 When organochlorine pesticides exist as complex mixtures, the individual compounds may be difficult to distinguish. High, low, or otherwise unreliable results may be obtained through misidentification and/or one compound obscuring another of lesser concentration. Provisions incorporated in this method are intended to minimize the occurrence of such interferences.

2. Summary

2.1 The method offers several analytical alternatives, dependent on the analyst's assessment of the nature and extent of interferences and/or the complexity of the pesticide mixtures found. Specifically, the procedure describes the use of an effective co-solvent for efficient sample extraction; provides, through use of column chromatography

and liquid-liquid partition, methods for elimination of non-pesticide interferences and the pre-separation of pesticide mixtures. Identification is made by selective gas chromatographic separations and may be corroborated through the use of two or more unlike columns. Detection and measurement is accomplished by electron capture, microcoulometric or electrolytic conductivity gas chromatography. Results are reported in micrograms per liter.

2.2 This method is recommended for use only by experienced pesticide analysts or under the close supervision of such qualified persons.

3. 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 of these materials must be demonstrated to be free from interferences under the conditions of the analysis. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Refer to Part I, Sections 1.4 and 1.5, (1).

3.2 The interferences in industrial effluents are high and varied and often pose great difficulty in obtaining accurate and precise measurement of organochlorine pesticides. Sample clean-up procedures are generally required and may result in the loss of certain organochlorine pesticides. Therefore, great care should be exercised in the selection and use of methods for eliminating or minimizing interferences. It is not possible to describe procedures for overcoming all of the interferences that may be encountered in industrial effluents.

3.3 Polychlorinated Biphenyls (PCB's) - Special attention is called to industrial plasticizers and hydraulic fluids such as the PCB's which are a potential source of interference in pesticide analysis. The presence of PCB's is indicated by a large number of partially resolved or unresolved peaks which may occur throughout the entire chromatogram. Particularly severe PCB interference will require special separation procedures (2,3).

3.4 Phthalate Esters - These compounds, widely used as plasticizers, respond to the electron capture detector and are a source of interference in the determination of organochlorine pesticides using this detector. Water leaches these materials from plastics, such as polyethylene bottles and tygon tubing. The presence of phthalate esters is implicated in samples that respond to electron capture but not to the microcoulometric or electrolytic conductivity halogen detectors or to the flame photometric detector.

3.5 Organophosphorus Pesticides - A number of organophosphorus pesticides, such as those containing a nitro group, eg, parathion, also respond to the electron capture detector and may interfere with the determination of the organochlorine pesticides. Such compounds can be identified by their response to the flame photometric detector (4).

4. Apparatus and Materials

4.1 Gas Chromatograph - Equipped with glass lined injection port.

4.2 Detector Options:

4.2.1 Electron Capture - Radioactive (tritium or nickel 63)

4.2.2 Microcoulometric Titration

4.2.3 Electrolytic Conductivity

4.3 Recorder - Potentiometric strip chart (10 in.) compatible with the detector.

4.4 Gas Chromatographic Column Materials:

4.4.1 Tubing - Pyrex (180 cm long x 4 mm ID)

4.4.2 Glass Wool - Silanized

4.4.3 Solid Support - Gas-Chrom Q (100-120 mesh)

4.4.4 Liquid Phases - Expressed as weight percent coated on solid support.

4.4.4.1 OV-1, 3%

4.4.4.2 OV-210, 5%

4.4.4.3 OV-17, 1.5% plus QF-1, 1.95%

4.4.4.4 QF-1, 6% plus SE-30, 4%

4.5 Kuderna-Danish (K-D) Glassware (Kontes)

4.5.1 Snyder Column - three ball (macro) and two ball (micro)

4.5.2 Evaporative Flasks - 500 ml

4.5.3 Receiver Ampuls - 10 ml, graduated

4.5.4 Ampul Stoppers

4.6 Chromatographic Column - Chromaflex (400 mm long x 19 mm ID) with coarse fritted plate on bottom and Teflon stopcock; 250 ml reservoir bulb at top of column with flared out funnel shape at top of bulb - a special order (Kontes K-420540-9011).

4.7 Chromatographic Column - pyrex (approximately 400 mm long x 20 mm ID) with coarse fritted plate on bottom.

4.8 Micro Syringes - 10, 25, 50 and 100 µl

4.9 Separatory Funnels - 125 ml, 1000 ml and 2000 ml with Teflon stopcock.

4.10 Blender - High speed, glass or stainless steel cup.

4.11 Graduated cylinders - 100 and 250 ml

4.12 Florisil - PR Grade (60-100 mesh); purchase activated at 1250 F and store in the dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch overnight at 130 C in foil-covered glass container. Determine lauric-acid value (See Appendix I).

5. Reagents, Solvents, and Standards

5.1 Ferrous Sulfate - (ACS) 30% solution in distilled water.

5.2 Potassium Iodide - (ACS) 10% solution in distilled water.

5.3 Sodium Chloride - (ACS) Saturated solution in distilled water (pre-rinse NaCl with hexane).

5.4 Sodium Hydroxide - (ACS) 10 N in distilled water.

5.5 Sodium Sulfate - (ACS) Granular, anhydrous (conditioned @ 400 C for 4 hrs).

5.6 Sulfuric Acid - (ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.7 Diethyl Ether - Nanograde, redistilled in glass, if necessary.

5.7.1 Must contain 2% alcohol and be free of peroxides by following test: To 10 ml of ether in glass-stoppered cylinder previously rinsed with ether, add one ml of freshly prepared 10% KI solution. Shake and let stand one minute. No yellow color should be observed in either layer.

5.7.2 Decompose ether peroxides by adding 40 g of 30% ferrous sulfate solution to each liter of solvent. CAUTION: Reaction may be vigorous if the solvent contains a high concentration of peroxides.

5.7.3 Distill deperoxidized ether in glass and add 2% ethanol.

5.8 Acetonitrile, Hexane, Methanol, Methylene Chloride, Petroleum Ether (boiling range 30-60 C) - nanograde, redistill in glass if necessary

5.9 Pesticide Standards - Reference grade.

6. Calibration

6.1 Gas chromatographic operating conditions are considered acceptable if the response to dicapthon is at least 50% of full scale when $\leq$ 0.06 ng is injected for electron capture detection and $\leq$ 100 ng is injected for microcoulometric or electrolytic conductivity detection. For all quantitative measurements, the detector must be operated within its linear response range and the detector noise level should be less than 2% of full scale.

6.2 Standards are injected frequently as a check on the stability of operating conditions. Gas chromatograms of several standard pesticides are shown in Figures 1, 2, 3 and 4 and provide reference operating conditions for the four recommended columns.

6.3 The elution order and retention ratios of various organochlorine pesticides are provided in Table 1, as a guide.

7. Quality Control

7.1 Duplicate and spiked sample analyses are recommended as quality control checks. When the routine occurrence of a pesticide is being observed, the use of quality control charts is recommended (5).

7.2 Each time a set of samples is extracted, a method blank is determined on a volume of distilled water equivalent to that used to dilute the sample.

8. Sample Preparation

8.1 Blend the sample if suspended matter is present and adjust pH to near neutral (pH 6.5-7.5) with 50% sulfuric acid or 10 N sodium hydroxide.

8.2 For a sensitivity requirement of 1 µg/1, when using microcoulometric or electrolytic conductivity methods for detection, 100 ml or more of sample will be required for analysis. If interferences pose no problem, the sensitivity of the electron capture detector should permit as little as 50 ml of sample to be used. Background information on the extent and nature of interferences will assist the analyst in choosing the required sample size and preferred detector.

8.3 Quantitatively transfer the proper aliquot into a two-liter separatory funnel and dilute to one liter.

9. Extraction

9.1 Add 60 ml of 15% methylene chloride in hexane (v:v) to the sample in the separatory funnel and shake vigorously for two minutes.

9.2 Allow the mixed solvent to separate from the sample, then draw the water into a one-liter Erlenmeyer flask. Pour the organic layer into a 100 ml beaker and then pass it through a column containing 3-4 inches of anhydrous sodium sulfate, and collect it in a 500 ml K-D flask equipped with a 10 ml ampul. Return the water phase to the separatory funnel. Rinse the Erlenmeyer flask with a second 60 ml volume of solvent; add the solvent to the separatory funnel and complete the extraction procedure a second time. Perform a third extraction in the same manner.

9.3 Concentrate the extract in the K-D evaporator on a hot water bath.

9.4 Analyze by gas chromatography unless a need for cleanup is indicated. (See Section 10).

10. Clean-up and Separation Procedures

10.1 Interferences in the form of distinct peaks and/or high background in the initial gas chromatographic analysis, as well as the physical characteristics of the extract (color, cloudiness, viscosity) and background knowledge of the sample will indicate whether clean-up is required. When these interfere with measurement of the pesticides, or affect column life or detector sensitivity, proceed as directed below.

10.2 Acetonitrile Partition - This procedure is used to isolate fats and oils from the sample extracts. It should be noted that not all pesticides are quantitatively recovered by this procedure. The analyst must be aware of this and demonstrate the efficiency of the partitioning for specific pesticides. Of the pesticides listed in Scope (1.2) only mirex is not efficiently recovered.

10.2.1 Quantitatively transfer the previously concentrated extract to a 125 ml separatory funnel with enough hexane to bring the final volume to 15 ml. Extract the sample four times by shaking vigorously for one minute with 30 ml portions of hexane-saturated acetonitrile.

10.2.2 Combine and transfer the acetonitrile phases to a one-liter separatory funnel and add 650 ml of distilled water and 40 ml of saturated sodium chloride solution. Mix thoroughly for 30-45 seconds. Extract with two 100 ml portions of

hexane by vigorously shaking about 15 seconds.

10.2.3 Combine the hexane extracts in a one-liter separatory funnel and wash with two 100 ml portions of distilled water. Discard the water layer and pour the hexane layer through a 3-4 inch anhydrous sodium sulfate column into a 500 ml K-D flask equipped with a 10 ml ampul. Rinse the separatory funnel and column with three 10 ml portions of hexane.

10.2.4 Concentrate the extracts to 6-10 ml in the K-D evaporator in a hot water bath.

10.2.5 Analyze by gas chromatography unless a need for further cleanup is indicated.

10.3 Florisil Column Adsorption Chromatography

10.3.1 Adjust the sample extract volume to 10 ml.

10.3.2 Place a charge of activated Florisil (weight determined by lauric-acid value, see Appendix I) in a Chromaflex column. After settling the Florisil by tapping the column, add about one-half inch layer of anhydrous granular sodium sulfate to the top.

10.3.3 Pre-elute the column, after cooling, with 50-60 ml of petroleum ether. Discard the eluate and just prior to exposure of the sulfate layer to air, quantitatively transfer the sample extract into the column by decantation and subsequent petroleum ether washings. Adjust the elution rate to about 5 ml per minute and, separately, collect up to three eluates in 500 ml K-D flasks equipped with 10 ml ampuls. (See Eluate Composition 10.4).

Perform the first elution with 200 ml of 6% ethyl ether in petroleum ether, and the second elution with 200 ml of 15% ethyl ether in petroleum ether. Perform the third elution with 200 ml of 50% ethyl ether - petroleum ether and the fourth elution with 200 ml of 100% ethyl ether.

10.3.4 Concentrate the eluates to 6-10 ml in the K-D evaporator in a hot water bath.

10.3.5 Analyze by gas chromatography.

10.4 Eluate Composition - By using an equivalent quantity of any batch of Florisil as determined by its lauric acid value, the pesticides will be separated into the eluates indicated below:

6% Eluate

Aldrin	DDT	Pentachloro-nitrobenzene
BHC	Heptachlor	Strobane
Chlordane	Heptachlor Epoxide	Toxaphene
DDD	Lindane	Trifluralin
DDE	Methoxychlor	PCB's
	Mirex	

15% Eluate

Endosulfan I
Endrin
Dieldrin
Dichloran
Phthalate esters

50% Eluate

Endosulfan II
Captan

Certain thiophosphate pesticides will occur in each of the above fractions as well as the 100% fraction. For additional information regarding eluate composition, refer to the FDA Pesticide Analytical Manual (6).

11. Calculation of Results

11.1 Determine the pesticide concentration by using the absolute calibration procedure described below or the relative calibration procedure described in Part I, Section 3.4.2. (1).

(1) $$\text{Micrograms/liter} = \frac{(A)\ (B)\ (V_t)}{(V_i)\ (V_s)}$$

$A = \frac{\text{ng standard}}{\text{Standard area}}$

B = Sample aliquot area

V_i = Volume of extract injected (µl)

V_t = Volume of total extract (µl)

V_s = Volume of water extracted (ml)

12. Reporting Results

12.1 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

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Table 1

RETENTION RATIOS OF VARIOUS ORGANOCHLORINE PESTICIDES RELATIVE TO ALDRIN

Liquid Phase[1]	1.5% OV-17 + 1.95% QF-1	5% OV-210	3% OV-1	6% QF-1 + 4% SE-30
Column Temp.	200 C	180 C	180 C	200 C
Argon/Methane Carrier Flow	60 ml/min	70 ml/min	70 ml/min	60 ml/min
Pesticide	RR	RR	RR	RR
Trifluralin	0.39	1.11	0.33	0.57
α-BHC	0.54	0.64	0.35	0.49
PCNB	0.68	0.85	0.49	0.63
Lindane	0.69	0.81	0.44	0.60
Dichloran	0.77	1.29	0.49	0.70
Heptachlor	0.82	0.87	0.78	0.83
Aldrin	1.00	1.00	1.00	1.00
Heptachlor Epoxide	1.54	1.93	1.28	1.43
Endosulfan I	1.95	2.48	1.62	1.79
p,p'-DDE	2.23	2.10	2.00	1.82
Dieldrin	2.40	3.00	1.93	2.12
Captan	2.59	4.09	1.22	1.94
Endrin	2.93	3.56	2.18	2.42
o,p'-DDT	3.16	2.70	2.69	2.39
p,p'-DDD	3.48	3.75	2.61	2.55
Endosulfan II	3.59	4.59	2.25	2.72
p,p'-DDT	4.18	4.07	3.50	3.12
Mirex	6.1	3.78	6.6	4.79
Methoxychlor	7.6	6.5	5.7	4.60
Aldrin (Min absolute)	3.5	2.6	4.0	5.6

[1]All columns glass, 180 cm X 4 mm ID, solid support Gas-Chrom Q (100/120 mesh)

APPENDIX 1

13. Standardization of Florisil Column by Weight Adjustment Based on Adsorption of Lauric Acid.

13.1 A rapid method for determining adsorptive capacity of Florisil is based on adsorption of lauric acid from hexane solution (6) (8). An excess of lauric acid is used and amount not adsorbed is measured by alkali titration. Weight of lauric acid adsorbed is used to calculate, by simple proportion, equivalent quantities of Florisil for batches having different adsorptive capacities.

13.2 Apparatus

13.2.1 Buret. -- 25 ml with 1/10 ml graduations.

13.2.2 Erlenmeyer flasks. -- 125 ml narrow mouth and 25 ml, glass stoppered.

13.2.3 Pipet. -- 10 and 20 ml transfer.

13.2.4 Volumetric flasks. -- 500 ml.

13.3 Reagents and Solvents

13.3.1 Alcohol, ethyl. -- USP or absolute, neutralized to phenolphthalein.

13.3.2 Hexane. -- Distilled from all glass apparatus.

13.3.3 Lauric acid. --Purified, CP.

13.3.4 Lauric acid solution. -- Transfer 10.000 g lauric acid to 500 ml volumetric flask, dissolve in hexane, and dilute to 500 ml (1 ml = 20 mg).

13.3.5 Phenolphthalein Indicator. -- Dissolve 1 g in alcohol and dilute to 100 ml.

13.3.6 Sodium hydroxide. -- Dissolve 20 g NaOH (pellets, reagent grade) in water and dilute to 500 ml (1N). Dilute 25 ml 1N NaOH to 500 ml with water (0.05N). Standardize as follows: Weigh 100-200 mg lauric acid into 125 ml Erlenmeyer flask. Add 50 ml neutralized ethyl alcohol and 3 drops phenolphthalein indicator; titrate to permanent end point. Calculate mg lauric acid/ml 0.05 N NaOH (about 10 mg/ml).

13.4 Procedure

13.4.1 Transfer 2.000 g Florisil to 25 ml glass stoppered Erlenmeyer flasks. Cover loosely with aluminum foil and heat overnight at 130°C. Stopper, cool to room temperature, add 20.0 ml lauric acid solution (400 mg), stopper, and shake occasionally for 15 min. Let adsorbent settle and pipet 10.0 ml of supernatant into 125 ml Erlenmeyer flask. Avoid inclusion of any Florisil.

13.4.2 Add 50 ml neutral alcohol and 3 drops indicator solution; titrate with 0.05N to a permanent end point.

13.5 Calculation of Lauric Acid Value and Adjustment of Column Weight

13.5.1 Calculate amount of lauric acid adsorbed on Florisil as follows:

Lauric Acid value = mg lauric acid/g Florisil = 200 - (ml required for titration X mg lauric acid/ml 0.05N NaOH).

13.5.2 To obtain an equivalent quantity of any batch of Florisil, divide 110 by lauric acid value for that batch and multiply by 20 g. Verify proper elution of pesticides by 13.6.

13.6 Test for Proper Elution Pattern and Recovery of Pesticides: Prepare a test mixture containing aldrin, heptachlor epoxide, p,p'-DDE, dieldrin, Parathion and malathion. Dieldrin and Parathion should elute in the 15% eluate; all but a trace of malathion in the 50% eluate and the others in the 6% eluate.

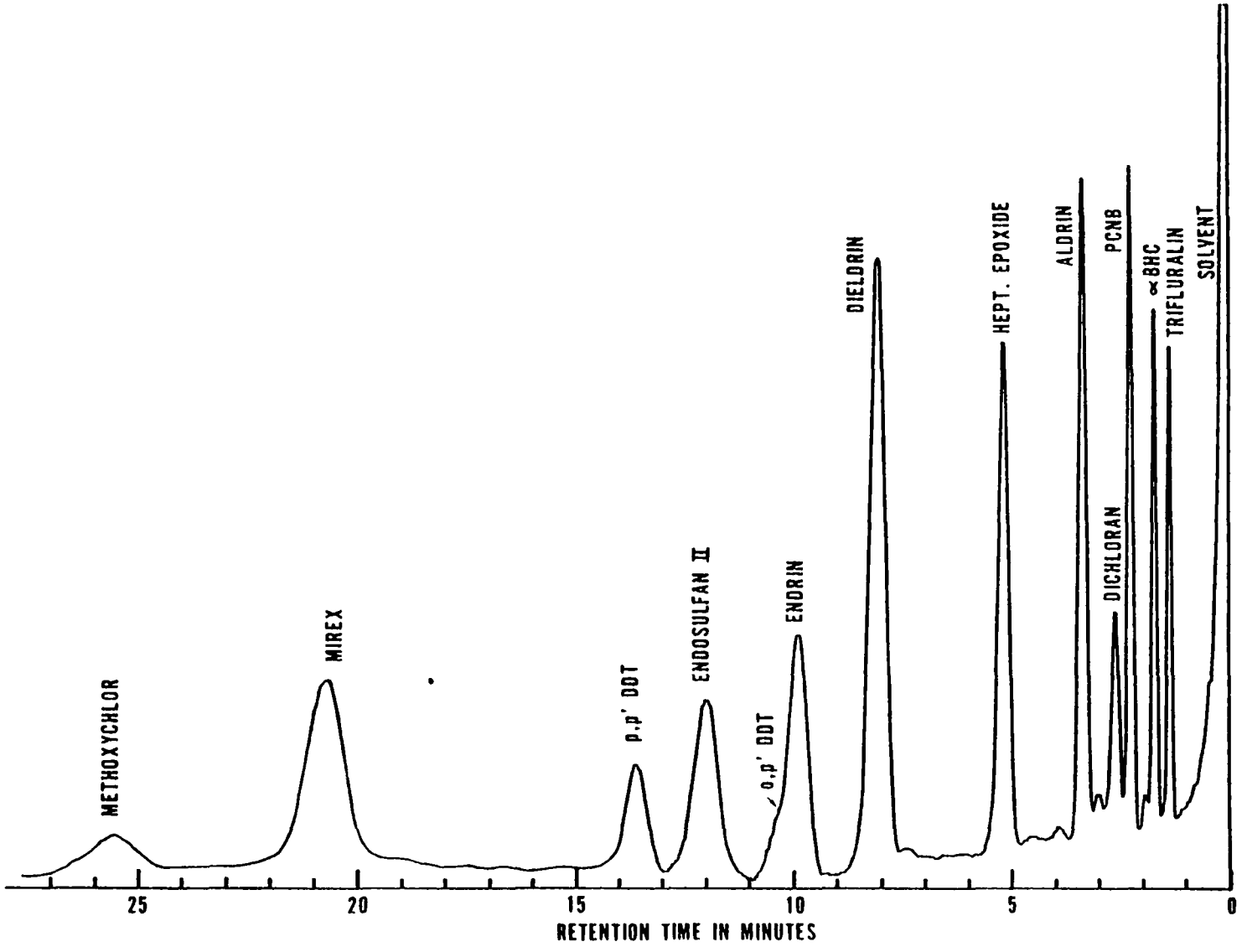

Figure 1. Column Packing: 1.5% OV-17 + 1.95% QF-1, Carrier Gas: Argon/Methane at 60 ml/min, Column Temperature: 200 C, Detector: Electron Capture.

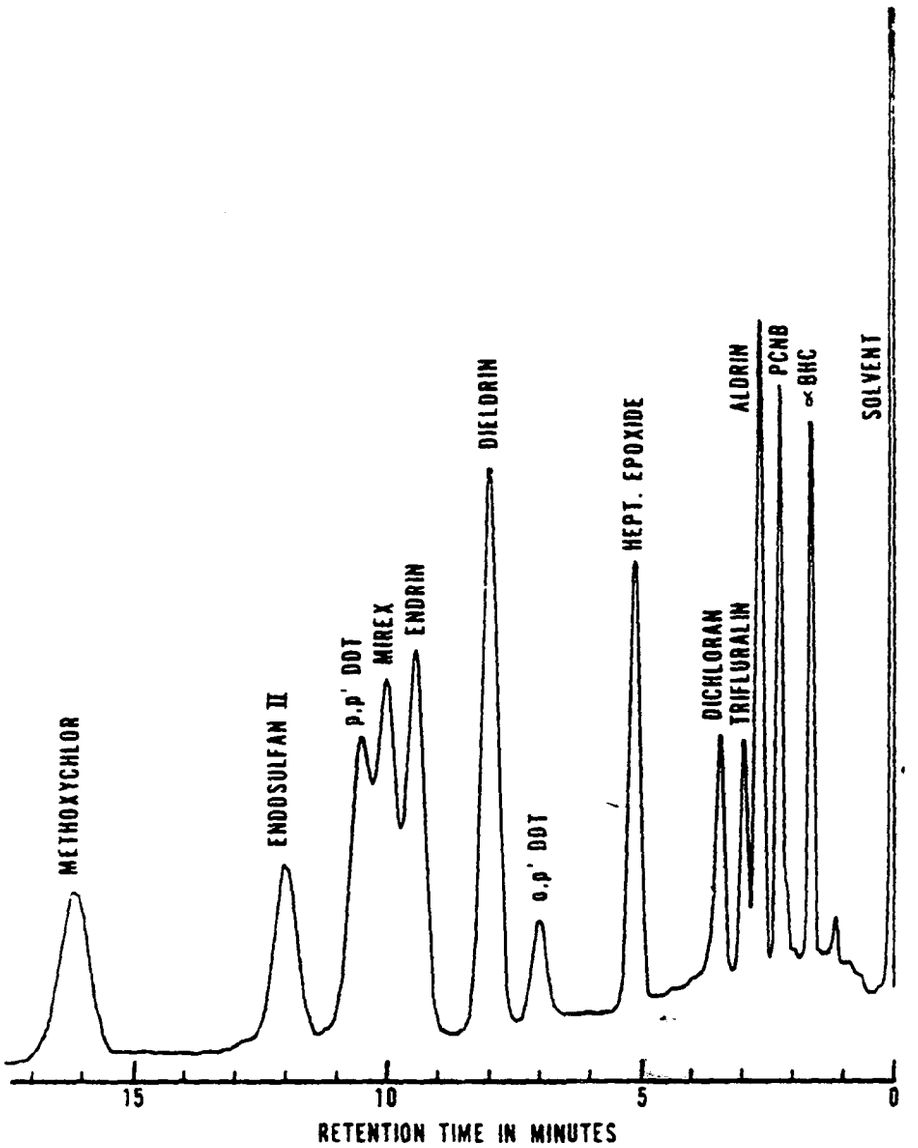

Figure 2. Column Packing: 5% OV-210, Carrier Gas: Argon/Methane at 70 ml/min, Column Temperature: 180 C, Detector: Electron Capture.

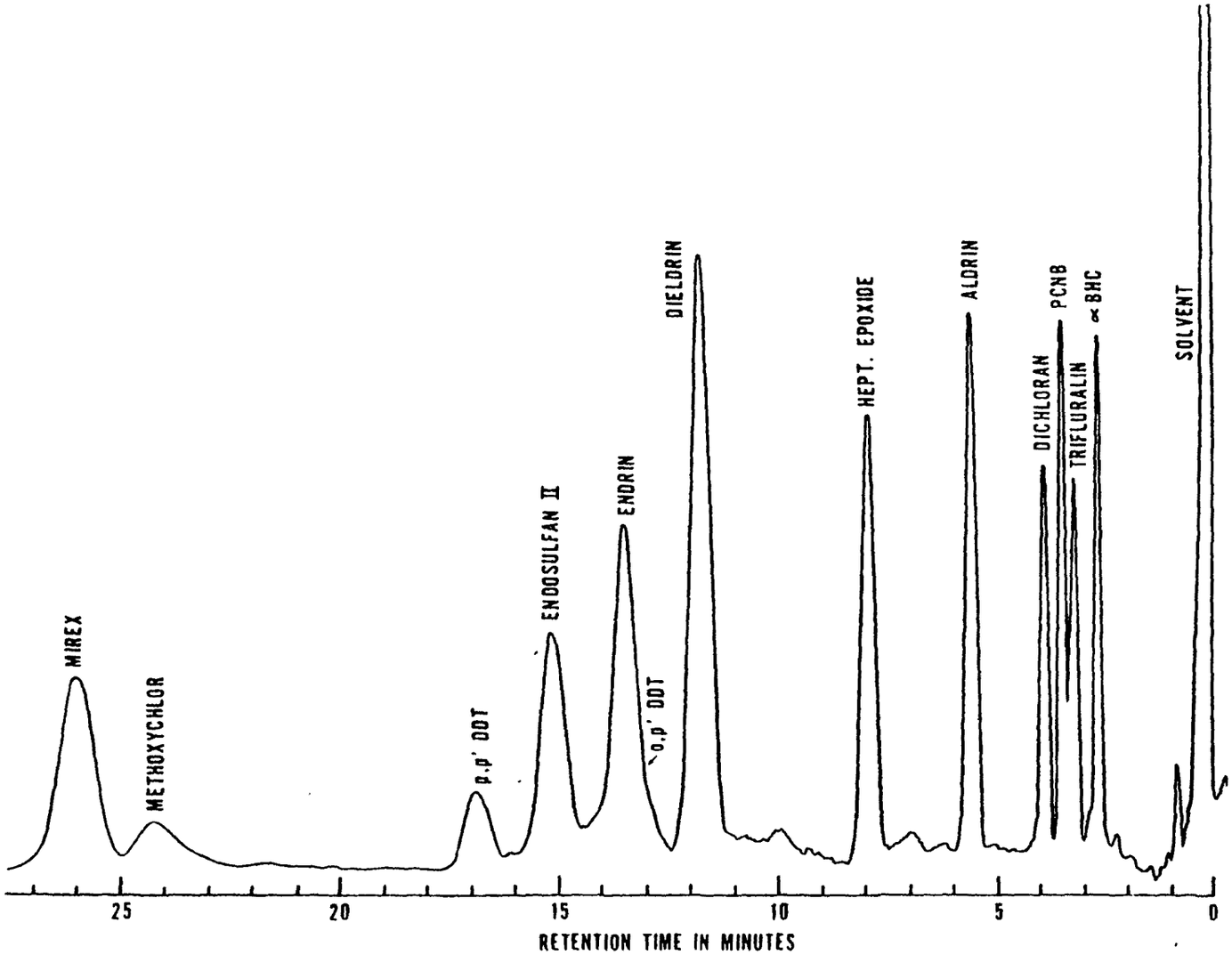

Figure 3. Column Packing: 6% QF-1 + 4% SE-30, Carrier Gas: Argon/Methane at 60 ml/min, Column Temperature: 200 C, Detector: Electron Capture.

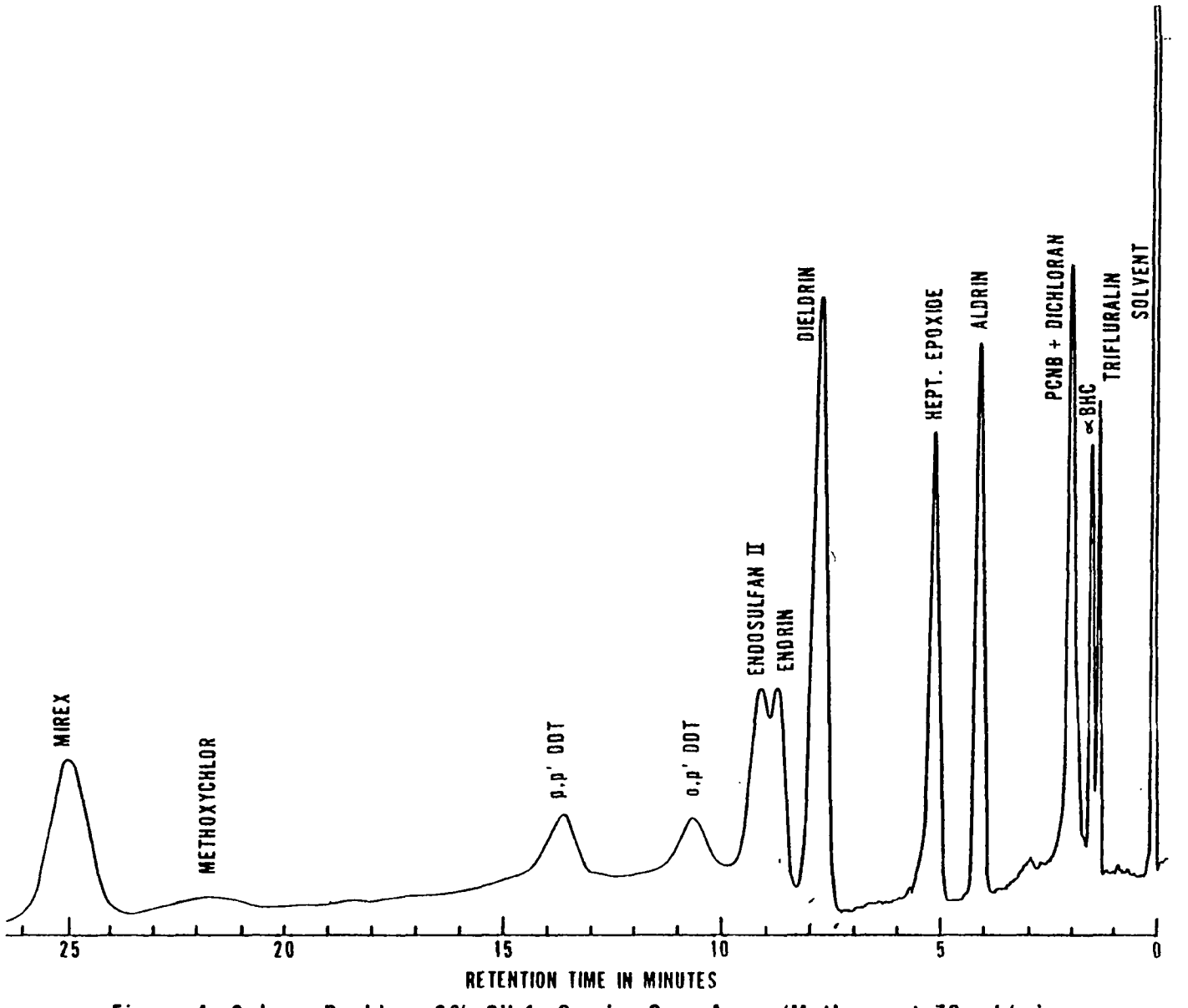

Figure 4. Column Packing: 3% OV-1, Carrier Gas: Argon/Methane at 70 ml/min, Column Temperature: 180 C, Detector: Electron Capture.

REFERENCE NO. 7

METHODS FOR CHEMICAL ANALYSIS OF WATER AND WASTES

REFERENCE NO. 8

DETERMINING SELENIUM

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DETERMINING SELENIUM IN WATER, WASTEWATER, SEDIMENT, AND SLUDGE BY FLAMELESS ATOMIC ABSORPTION SPECTROSCOPY

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ABSTRACT

A method has been developed for the determination of selenium in freshwater, wastewater, sediment, and sludge by flameless atomic absorption spectroscopy. A simple and rapid sample preparation is given with a description of the interferences that affect the analysis. Nickel nitrate is added to both standards and samples to prevent losses by volatilization. The method demonstrates good precision with day-to-day variation of the absorbance values at the 0.25 and 2.5 nanogram level (25 µl of 10 and 100 µg Se/l) varying only ±11.6% and ±4.1% respectively, at the 95% confidence level. The sensitivity of the method is 20 picograms which for many tap, surface, and well waters extends the detection limit to 0.2 µg Se/l without the use of scale expansion.

RESUME

On a développé une méthode pour la détermination du sélénium dans des eaux fraîches et résiduelles, des sédiments et des boues par spectroscopie d'absorption atomique sans flamme. On donne une méthode simple et rapide pour la préparation des échantillons ainsi qu'une description des interférences qui affectent l'analyse.

On fait un ajout de nitrate de nickel aux standards et aux échantillons de manière à empêcher des pertes par volatilisation. La méthode offre une bonne précision avec une variation des valeurs d'absorbance de jour en jour de ± 11,6% et ± 4,1% seulement au seuil de confiance de 95% et ce respectivement pour des valeurs de 0,25 et 2,5 nanogrammes (25 µl de 10 et 100 µg Se/l). La sensibilité de la méthode est de 20 picogrammes, ce qui pour de nombreuses eaux de distribution, de surface et de puits donne une détection limite de 0,2 µg Se/l, sans usage d'expansion d'échelle.

ZUSAMMENFASSUNG

Eine Methode zur Bestimmung von Selen in Frischwasser, Abwasser, Sedimenten und Klärschlamm wurde mittels der flammenlosen Atomabsorptions - Spektroskopie entwickelt. Es wird auf eine einfache und rasche Probenaufbereitung hingewiesen und die, die Analyse beeinflussenden Interferenzen angegeben. Nickelnitrat wird sowohl zu den Standards alsauch zu den Proben zugesetzt, um eventuelle Verluste durch Flüchtigkeit zu vermeiden. Die Methode zeigt für Extinktionswerte beim 0,25 und 2,5 ng-Niveau (25 µl von 10 und 100 µg Se/l) eine gute Präzision und Reproduzierbarkeit, mit Abweichungen von nur ±11,6% beziehungsweise ±4,1%, bei einer 95%igen Sicherheit. Die Empfindlichkeit der Methode von 20 pg erweitert die Nachweisgrenze bis 0,2 µg Se/l für viele Leitungs.-Oberflächen.-und Quellenwässer, ohne der Anwendung einer Skalendehnung.

INTRODUCTION

The analytical determination of selenium has long been a problem to the analytical chemist. It is similar to arsenic in toxicity and reactivity yet is probably much more difficult to detect and measure. The procedure given in *Standard Methods for the Examination of Water and Wastewater*, 13th Ed., 1971, is time-consuming, subject to many interferences, and relatively insensitive thus requiring a large volume of sample. Therefore, it is often omitted from routine analysis. Additionally, the colorimetric reagent often used (diaminobenzidine) has been placed on the possible carcinogenic listing.

The selenium concentration of most finished waters is less than 10 µg/l. However, the use of selenium in industry is growing. A major use of selenium is in the glass industry to color glass a deep red and to neutralize iron color. Selenium is known to be present in almost all types of paper. Selenium may be present in soils both as selenite and selenate. Thus, it is likely to be found in surface waters. Although trace amounts of selenium have been shown to be nutritionally beneficial in some animal diets, exposure to higher concentrations produces toxic effects. There are also some implications that selenium is a carcinogen.

In addition to the four valence states in which selenium may exist, a variety of organo-selenium compounds is known. Therefore, to ensure measurement of total selenium, any method devised must include an oxidation step. During this digestion, it is most important to maintain oxidizing conditions. Inorganic selenium is not appreciably volatilized during digestion in a mixture of nitric and perchloric acids (1, 2, 3, 4), except in the presence of such a large excess of organic material that charring occurs (3, 4). In general, selenium may be lost from acid selenite solutions by reducing but not by oxidizing agents.

In attempting to avoid volatilization losses, several methods effected dissolution of the sample through combustion with oxygen in closed systems (1, 5, 6, 7). This can be done either with a Schoniger combustion flask or in a Parr bomb. Watkinson (8), after comparing wet oxidation with the oxygen flask combustion, found no significant difference between the results of the two methods. He preferred oxidation with nitric and perchloric acids. The use of perchloric acid, however, is discouraged because of safety reasons.

Since most natural waters and waste effluents contain low concentrations of selenium, conventional atomic absorption has not been used for the analysis because of its relatively poor sensitivity. Since it forms a hydride similar to arsenic, several investigators have applied the arsine-type procedure with subsequent introduction in an argon-hydrogen flame to selenium (9). This technique has the advantage of eliminating interference resulting from the matrix effect and improving the detection limit. Many problems, however, have been encountered in determining selenium in domestic and industrial wastewaters particularly the interference of organics, high copper concentrations, and difficulty in forming the hydride.

With the advent of flameless atomization devices and electrodeless discharge lamps the analytical working range for many elements has been extended.

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Baird *et al.* (10), recently reported a flameless AAS method for the determination of selenium in wastewater employing a carbon rod analyzer. The obvious advantage of this mode of analysis is the absence of the usual high levels of flame background normally responsible for decreased sensitivity. Baird did observe the need for a preliminary digestion with nitric and perchloric acid to oxidize organic material and solubilize the selenium before injections into the carbon rod. Replicate analyses of samples containing approximately 10 µg of selenium per liter gave a relative standard deviation of 6.8%. Because of the safety factor, the authors of this paper prefer a digestion step using a combination of nitric acid-hydrogen peroxide. This combination allows the integrity of the sample to be broken down and all of the selenium to be solubilized while a condition of oxidation is maintained. Complete ashing occurs during the charring step after the sample has been injected into the furnace.

Because of its volatility, the possible loss of selenium has been a point of concern in flameless analysis. In the development of a furnace method for the analysis of selenium in biological materials, Ediger (11, 12) determined that the addition of nickel nitrate prior to the drying step produces a condition where high charring temperatures (1200° to 1500°C) can be tolerated without the loss of selenium. This condition facilitates complete ashing and the removal of some matrix constituents which may cause subsequent interference during the atomization. Welcher, *et al.* (13) have also demonstrated the stability of selenium in the presence of nickel or other heavy metals in the determination of trace elements in high temperature alloys. Recently, Henn (14) demonstrated the same effect with the use of molybdenum after separation of the selenium from metallic interferences with a cation exchange resin.

This paper describes a method incorporating the nitric acid-hydrogen peroxide digestion procedure, followed by the addition of nickel nitrate and the use of the HGA-2000 Graphite Furnace in connection with a selenium EDL for the determination of selenium in water, wastewater, sediments, and sludges while focusing on the problems encountered during the analysis.

EQUIPMENT

A Perkin-Elmer Model 503 atomic absorption spectrophotometer equipped with a Perkin-Elmer Model HGA-2000 Graphite Furnace, a Deuterium Background Corrector, and a Perkin-Elmer selenium Electrodeless Discharge Lamp (EDL) was used for the analysis. The spectrophotometer was operated in the peak read mode. A Perkin-Elmer Model 056 recorder on 10 millivolt span was used to record the absorbance signals. The Deuterium Background Corrector was used to compensate for non-specific absorption using nitrogen at a flow rate of 2 liters/min to purge the optics. The selenium EDL was operated at 9 watts, with a wavelength setting of 196.0 nm and a spectral slit width of 0.7 nm. All equipment requiring 120 volts was operated on regulated voltage with the spectrophotometer connected to a Stabiline saturable reactor autotransformer voltage regulator to insure stable power.

The HGA-2000 Graphite Furnace was programmed for drying at 125°C (with varying times depending on the volume of aliquot injected): 30-sec charring at 1500°C*; and 10-sec atomization at 2700°C. Argon was used as the furnace purge gas at a flow rate of 3 divisions, and the flow was interrupted automatically during atomization.

Drying times of 20 sec were used for volumes of 5 and 10 µl: 30 sec for 25 µl; 50 sec for 50 µl; 65 sec for 75 µl; and 80 sec for 100 µl.

Eppendorf microliter pipets with disposable tips were used to inject the samples into the furnace.

REAGENTS AND STANDARDS

Nitric Acid

(HNO_3), concentrated, ACS reagent grade, redistilled.

Hydrogen Peroxide

(H_2O_2), 30%, ACS reagent grade.

Standard Selenium Solution

A stock solution of 1000 mg Se/l was prepared by dissolving 0.3453 grams of selenous acid (actual assay 94.6% H_2SeO_3) in 200 ml of deionized distilled water. Dilute working standards (1, 2, 5, 10, 40, 50 and 100 µg Se/l were prepared from a diluted stock solution of 10 mg Se/l by withdrawing the appropriate aliquot, adding to it 1 ml of conc. HNO_3, 2 ml 30% H_2O_2 and diluting to 100 ml with deionized distilled water.

Nickel Nitrate

(1% Ni solution) — Dissolve 4.956 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in 100 ml of deionized distilled water.

Nickel Nitrate

(5% Ni Solution) — Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in 100 ml of deionized distilled water.

SAMPLE PREPARATION AND PROCEDURE

Detailed procedures on sample preparation and the final concentration of nickel depend on sample type, matrix, and concentration of selenium to be determined. In all cases where total selenium is to be determined, the sample is subjected to vigorous oxidation to solubilize the selenium.

Well and Surface Water

Transfer 100 ml of well-mixed sample to a 250-ml Griffin beaker, add 3 ml conc. redistilled HNO_3 and 5 ml 30% H_2O_2. Heat for one hr at 95°C or until the volume is slightly less than 50 ml. Cool and bring back to 50 ml with deionized distilled water. 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 deionized distilled water. The sample is now ready for analysis.

Since the nickel concentration is 0.1%, the sample should be compared to a standard curve constructed from standards also containing 0.1% nickel. The aliquot size used for injection into the furnace should be the same for both samples and standards. Recommended volume for this type of sample is 25 to 100 µl.

To verify the absence of matrix or chemical interference, an aliquot of the digest solution should be spiked with a known amount of selenium, nickel nitrate added, and analyzed in the same manner. The actual signal compared to the expected response will indicate the presence of any significant interference. Those samples where interference is detected must either have the interference reduced by dilution or be analyzed by the method of standard additions. (See discussion on interferences.)

Many surface water samples having low dissolved solids (400 mg/l) may be concentrated 5X during the digestion step. Even though this technique extends the detection

*Since there are differences between individual furnaces and the reading and setting of the maximum allowable charring temperature, each furnace should be checked to determine the maximum charring temperature before beginning the analysis.

limit, the solution must still be checked for interference by spiking an aliquot of the concentrate and performing the analysis.

Samples with sulfate concentration higher than 200 mg/l should be analyzed in the presence of 1% Ni. Samples are prepared and analyzed as previously described except the addition of nickel nitrate should be 2.0 ml of the 5% Ni solution diluted to 10 ml. Results should be determined from a standard curve prepared from standards containing 1% Ni.

Industrial Waste Effluent

Sample should be prepared in the same manner as surface water, but the nickel concentration in the final dilution should be 1%. Results of many industrial effluents can be determined from a standard curve, but again each must be checked for possible interferences before this assumption can be made. In some cases sample dilution may be required. A typical set of data from Se standards in a 1% Ni matrix is listed in Table I. If it is necessary to use the method of standard additions, the size of the aliquot used for injection into the furnace will depend on the reproducibility of signal response and the amount of interference encountered. An aliquot of 25 µl was used for the work on this type of sample as reported in this paper.

Sediments and Sludges

Weigh and transfer to a 250-ml Griffin beaker a 0.5-g portion of a sample which has been dried at 60°C, pulverized, and thoroughly mixed. Add 5 ml of conc. HNO_3 and cover with a watch glass. The sample should be heated at 95°C and refluxed to near dryness. Allow the sample to cool, add another 5 ml of conc. HNO_3 and repeat the digestion step. After the second reflux step has been completed, allow the sample to cool, add 3 ml of conc. HNO_3 and 10 ml 30% H_2O_2. Return the beaker to the hot plate for warming to start vigorous reaction. When the reaction has commenced, immediately remove the beaker from hot plate. After effervescence has subsided, return the covered beaker to the hot plate and reflux for 15 minutes. After cooling, dilute the sample to 50 ml with deionized distilled water. Mix and withdraw a 5-ml aliquot, to be diluted to 10 ml, for analysis by the method of standard additions. Each final solution should contain 1% Ni (2.0 ml of 5% Ni solution) and suspended solids should be permitted to settle before analysis. It is suggested that solutions used for analysis by the method of standard additions contain 5 ml of sample plus 15, 30, and 45 µg Se/l. Because the possibility of encountering severe interferences is greatest in this type of sample, a 5-µl aliquot should be used for furnace injection. A detection limit of 5 µg/g sample can be achieved with this method using a 5-µl injection.

ANALYTICAL PROCEDURE

The instrument should be operated using the conditions as listed in the section on Equipment. As previously mentioned, the size of the aliquot used for furnace injection will depend on the sample type as well as the matrix. When the method of standard additions is required, a linear curve over the entire range of the additions is necessary for the results to be considered valid.

The life and performance of the furnace tube using this method will mainly be affected by the number of analyses completed. Many tubes have lasted for more than 100 firings but it is recommended, because of varying sample types, that the tube be replaced after 100 firings. Prolonged use of a given tube will result in elevated values, sometimes exceeding the expected value by more than 10%; but since the increase is a gradual drift, there is no loss of precision in consecutive analyses. For those samples which have a complex matrix including metals of low volatility and requiring the 1% nickel matrix, a conditioning cleaning burn after each analysis may prove helpful. This can be accomplished by eliminating the drying and charring step, and atomizing at 2700°C for 15 sec without gas interrupt.

RESULTS AND DISCUSSION

Effect of Nickel

The addition of nickel to the sample serves three purposes. First, it is believed to form a stable selenide compound at the beginning of the char cycle thereby reducing the volatility of selenium. This allows the use of elevated charring temperature for complete ashing and volatilization of some possible interfering and non-specific absorbing substances. The second advantage of the nickel is the increase in sensitivity gained because of the enhancement effect. To demonstrate this effect a new graphite tube was placed in the furnace, and the charring temperature was set at 200°C. Average absorbances of 0.110 and 0.225 respectively were recorded for a 25-µl injection of a 40 µg Se/l solution first without, and then with the addition of nickel (1000 mg/l). The absorbance value (0.225) for the charring temperature of 200°C is, for all practical purposes, the same as when the charring temperature for the same selenium solution is raised to 1500°C (Abs=0.235). This comparison, with and without the nickel, indicates about a two-fold enhancement because of the nickel. This enhancement may be due to a decrease in the rate of atomization or a change in the efficiency of the atomization. Under the standard conditions given, a nickel concentration of 100 mg/l to 2000 mg/l gives a similar enhancement, but when the nickel concentration is increased to 10,000 mg/l, or 1%, the absorbance for 25 µl of a 40 µg Se/l solution drops to 0.170. Since the amount of nickel in the furnace during atomization is critical to the signal response, it must be controlled and the same quantity must be present for both standards and samples.

Thirdly, the nickel serves as a stable matrix for those tap, surface and well waters which have low concentrations of trace metals and sulfate ion, thereby permitting the use of a standard curve of the same nickel concentration.

Standard Curve

Table 1 shows the average absorbance and relative standard deviation values for a composite standard curve in a 0.1% Ni matrix over a concentration range of 5 to 100 µg Se/l. The volume of the aliquot used for the injection for each standard was 25 µl. These standard data are the result of values collected on 9 different days over a period of 3 weeks. The composite data reflect normal daily variations in instrumental parameters and the effect of different graphite tubes. Selenium is linear up to an absorbance value of 0.4 in a 0.1% nickel matrix. A working detection limit using this technique is 2 µg Se/l. This detection limit can be extended to 1 µg Se/l using a 100-µl aliquot injection or to as little as 0.2 µg Se/l if the sample is first concentrated five times by evaporation, and a 50-µl aliquot used for the injection. In both cases the concentration of the constituents in the sample matrix will be the determining factor. To verify this procedure and standard data, quality control check samples supplied by the Quality Assurance Branch of the Environmental Monitoring and

TABLE I
Selenium Standard Data in 0.1% Ni Matrix*

Se Concentration µg/liter	Average Absorbance	% Relative Std Deviation+
5	0.035	14.2
10	0.065	11.6
20	0.118	9.3
40	0.235	7.2
50	0.290	6.4
100	0.540	4.1

+At the 95% confidence level.

Selenium Standard Data in 1% Ni Matrix*

Se Concentration µg/liter	Average Absorbance
10	0.046
20	0.091
40	0.170
50	0.219
100	0.413

*25-µl sample aliquots.

Support Laboratory in Cincinnati were analyzed at the 4, 16, and 48 µg/l levels with recoveries of 90%, 97%, and 96% respectively.

Water Matrix — Sulfate Interference

A major concern of any analytical technique is the possible effect of the common minerals and anions present and their concentration on the analytical result. Table II lists a variety of parameters, their concentrations, and the selenium response observed. Examination of the data indicates an inverse relationship between the concentration of magnesium and sulfate and the selenium absorbance. Since it is known that a concentration of magnesium as high as 200 mg/l has no effect on the selenium response, the increase in the suppression of selenium is attributed to the increasing concentration of sulfate. Table III is also evidence of sulfate interference. Section (A) shows the effect of large concentrations of sulfate. Section (B) shows the effect in more detail over a small concentration range. Section (C) shows that the degree of the sulfate suppression can be reduced by increasing the amount of nickel present during the analysis. If the concentration of the nickel in the injection aliquot is increased to 1% (10,000 mg/l), an injection of 50 µg of sulfate (50 µl of 1000 mg SO_4/l) will only cause a 15% suppression to the signal generated by 1 nanogram of Se (25 µl of 40 µg Se/l). See Table V for a comparison.

Chloride and Nitrate Interference

Chloride and nitrate also affect selenium absorption. In both the 0.1% and the 1% nickel matrix, chloride concentrations greater than 800 mg/l cause a significant suppression (greater than 5%) of the absorbance. If the chloride is increased to 2000 mg/l, the suppression in 0.1% Ni and 1% Ni is approximately 15% and 30%, respectively. Thus an increase in nickel concentration does not decrease the suppressive effect of chloride, and therefore the method as described is not applicable to the analysis of seawater and brines.

In selenium solutions containing 1% v/v conc. HNO_3 there is an 80% reduction in the Se absorbance when the nickel is omitted, but in a 0.1% Ni matrix with 3% v/v conc. HNO_3 no reduction was observed. At levels above 3% nitrate, interference is encountered in the 0.1% nickel

TABLE II
Selenium Absorbance in Six Synthetic Surface Water Matrix Solutions of Various Concentrations*

Element, Anion or Measured Parameter	Distilled Water Solution	Concentration mg/liter 1	2	3	4	5	6
Calcium	0	90	180	180	180	360	360
Magnesium	0	21	25	41	41	41	82
Sodium	0	82	210	260	390	390	520
Potassium	0	16	32	32	32	63	63
Alkalinity	0	180	280	280	560	560	560
Chloride	0	174	350	350	350	700	700
Total hardness	0	310	550	630	600	1200	1240
Total dissolved solids	0	570	1200	1450	1760	2300	2900
Sulfate	0	84	260	440	440	440	870
Volume of Aliquot		Se Absorbance Values					
25 µl	0.122	—	—	0.104	0.100	0.109	0.097
% response	100%	—	—	85%	82%	89%	80%
50 µl	0.224	—	0.223	0.181	0.189	0.191	0.164
% response	100%	—	100%	81%	84%	85%	73%
100 µl	0.345	0.346	0.321	0.269	0.263	0.279	0.237
% response	100%	100%	93%	78%	76%	81%	69%

*Each of the 6 synthetic matrix solutions and the distilled water solution contained 20 µg Se/l in 0.1% Ni, 1% v/v conc. HNO_3, 2% v/v 30% H_2O_2.

TABLE III

Effect of Sulfate on Selenium Absorbance

	Volume of Sulfate Aliquot	Concentration mg SO_4/l	Total µg SO_4/Injection	Se Absorbance*	% Suppression of Se Absorbance
	0	0	0	0.30	—
	25 µl	500	13	0.22	27%
(A)	25 µl	1000	25	0.16	45%
	25 µl	2000	50	0.10	66%
	25 µl	4500	113	0.07	76%
				Se Absorbance†	
	0	0	0	0.230	—
	25 µl	270	6.8	0.230	0
	50 µl	180	9.0	0.215	6%
	25 µl	450	11.3	0.199	13%
(B)	50 µl	270	13.5	0.166	28%
	100 µl	180	18.0	0.140	39%
	50 µl	450	22.5	0.126	45%
	100 µl	270	27.0	0.107	53%
				Se Absorbance+	
	0 µl	0	0	0.230	—
	25 µl	450	11.3	0.212	8%
	50 µl	270	13.5	0.201	13%
(C)	50 µl	360	18.0	0.187	19%
	50 µl	450	22.5	0.168	27%
	75 µl	360	27.0	0.142	38%

*Se absorbance value and corresponding suppression is the result of a 25-µl injection of 50 µg Se/l in 0.1% Ni *(25 µg Ni/injection)*, 1% v/v conc. HNO_3 2% v/v 30% H_2O_2 with the listed quantity of sulfate pipetted on top of the Se injection.

†Same conditions as in * except 25 µl of 40 µg Se/l in 0.1% Ni *(25 µg Ni/injection)*, 1% v/v conc. HNO_3, 2% v/v 30% H_2O_2 was used for injection.

+Same conditions as in * except 50 µl of 20 µg Se/l in 0.1% Ni *(50 µg Ni/injection)*, 1% v/v conc. HNO_3, 2% v/v 30% H_2O_2 was used for injection.

matrix. Although this interference can be somewhat reduced and stabilized by the use of a longer charring cycle, concentrations of over 30,000 mg NO_3/l should be avoided.

Single Metal Interference

Table IV lists concentrations of single metal solutions and the degree to which these metals affect the Se absorbance in 0.1% Ni matrix. These approximate results are given as an indication of when the analyst can no longer reliably use a standard curve prepared in 0.1% Ni for the determination. Special attention should be given to the concentration of Fe, Sn, Si, Al, Mn, V, and Cr. Although seldom present at these concentrations in surface and tap water, there may be other types of environmental samples including sludges and sediments where these elements may exist in even greater concentrations than listed. It has been determined that increasing the concentration of the nickel to 1% decreases the suppressive effect of many metals. A comparison of the suppressive effect of some of the more critical metals in 0.1% and 1% nickel matrix is given in Table V. Although the selenium response is lower in 1% Ni than in 0.1% Ni when other metals are absent, the same is not necessarily true with the addition of these metals as evident in Table V. This phenomenon can be an advantage in eliminating large suppressive effects when analyzing samples with a complex matrix.

Since all of the metals tested have a concentration which can be tolerated without causing an interference, the determination of their composite effect at those concentrations both with and without the synthetic water matrix was important. Table VI lists the matrix parameters and trace metals, their concentrations, the affected selenium absorbance, and percent suppression in both 0.1% and 1% nickel solutions. In reviewing Table VI, it is apparent that there is a composite effect in 0.1% Ni but not in 1% Ni and that the combination of matrix and trace metals produces increased suppression in 0.1% Ni. This suppressive effect is strong evidence for using 1% nickel when analyzing samples with a complex matrix or ones that contain ions or trace metals at concentrations known to interfere. The sample may be analyzed using either a standard curve prepared in 1% Ni or, if necessary, by the technique of the method of standard additions. Whenever possible, and especially for tap water and clean, low dissolved solids surface water, the 0.1% nickel matrix should be used because of the added sensitivity.

Dissolved and Suspended Solids

In considering the effect of dissolved and suspended solids, it was determined that the nature or chemical composition of the solids rather than the physical state was the important factor. Also the amount of an interfering sub-

TABLE IV

Suppression Effects on Selenium Absorbance* of Single Metal Solutions+

Element	Concentration Which Has No Effect, mg/l	Concentration mg/l	Suppression	Concentration mg/l	Suppression
Ag	400	—		—	
Al	20	40	10%	200	65%
As	40	100	10%	400	50%
B	300	400	10%	—	
Ba	400	—		—	
Be	10	20	5%	40	20%
Cd	400	—		—	
Co	400	—		—	
Cr	50	100	10%	200	55%
Cu	100	200	10%	—	
Fe	4	10	10%	20	30%
Li	300	400	10%	—	
Mo	200	400	10%	—	
Mn	20	50	10%	200	50%
Ni	300	400	10%	—	
P	100	200	25%	400	75%
Pb	200	300	15%	400	30%
Sb	40	50	10%	100	20%
Si	10	20	10%	40	50%
Sn	2	4	10%	10	40%
Sr	400	—		—	
Ti	200	400	5%	—	
Tl	40	200	20%	400	30%
V	20	30	10%	100	30%
Zn	400	—		—	

*A 25-µl injection of 40 µg Se/l in 0.1% Ni, 1% v/v conc. HNO_3, 2% v/v 30% H_2O_2 was used for this comparative work.

+The approximate suppression values are the result of a 25-µl injection of the listed concentrations being pipetted on top of the selenium injection.

TABLE V

Comparison of Suppression Effects of Trace Metal Solutions on Selenium Absorbance in 0.1% Ni and 1% Ni Solutions

Trace Metal Solution	25 µl 40 µg Se/l in 0.1% Ni		25 µl 40 µg Se/l in 1% Ni	
	Absorbance	% Suppression	Absorbance	% Suppression
—	0.235	—	0.170	—
50 µl 100 mg Al/l	0.075	68	0.105	38
50 µl 100 mg Cr/l	0.095	60	0.140	18
50 µl 100 mg Cu/l	0.195	17	0.154	9
50 µl 100 mg Fe/l	0.120	49	0.126	26
50 µl 100 mg Si/l	0.025	89	0.086	49
50 µl 100 mg Sn/l	0.015	94	0.103	39
50 µl 100 mg V/l	0.085	64	0.148	13
50 µl 1000 mg SO_4/l	0.047	80	0.145	15

TABLE VI

Comparison of Selenium Absorbance in 0.1% Ni and 1% Ni Solutions Containing Synthetic Matrix and Trace Metals

Matrix		*Trace Metals*	
Element	*Conc.*	*Element*	*Conc.*
Calcium	180 mg/l	Sn	1 mg/l
Magnesium	20 mg/l	Be	2 mg/l
Sodium	190 mg/l	Fe	2 mg/l
Potassium	32 mg/l	Si	5 mg/l
Alkalinity	280 mg/l	V	5 mg/l
Chloride	350 mg/l	Mo	10 mg/l
Total hardness	600 mg/l	Al	20 mg/l
Total dissolved		As	20 mg/l
solids	1160 mg/l	Cu	20 mg/l
Sulfate	220 mg/l	Mn	20 mg/l
		P	20 mg/l

Solution Content	*Aliquot Injection Volume*	*0.1% Ni*		*1% Ni*	
		Se (30 µg/l) Absorbance	*% Enhanc. or Suppression*	*Se (24 µg/l) Absorbance*	*% Enhanc. or Suppression*
Se	25 µl	0.170	—	0.105	—
Se + matrix	25 µl	0.175	+ 3%	0.101	−4%
Se + metals	25 µl	0.150	−12%	0.111	+6%
Se + matrix + metals	25 µl	0.106	−38%	0.109	+4%

stance present during atomization is the important consideration — not whether injected as a dissolved or suspended solid. Review of Table II reveals that a change in total dissolved solids in the synthetic water matrix from 1450 mg/l to 2300 mg/l did not produce a significant difference in the selenium absorbance. Since the total dissolved solids for most surface water are below 2000 mg/l, solids should not be a problem in the analysis of water samples provided that the non-specific absorption does not exceed the background correction capability of the instrument.

Sample Analysis and Recovery Data

Analytical results and spike recovery on a variety of sample types are given in Table VII. The sample preparation used was that described in this paper. The results were determined from standard curves prepared in 0.1% and 1% nickel solutions, and by utilizing the method of standard additions.

CONCLUSION

This method utilizing the HGA-2000 Graphite Furnace provides a rapid procedure for analyzing a variety of water samples for selenium. After the sample preparation and solubilization, the samples are diluted in either 0.1% or 1% nickel matrix and compared to a standard curve of the same matrix to determine the result of the analysis. The method demonstrates satisfactory precision and is sufficiently sensitive with a working detection limit of 2 µg Se/l which can be extended to 0.2 µg Se/l. To detect sample matrix interference, spiked samples are analyzed and compared to the expected response of the spike. To compensate for matrix interferences and to analyze other types of environmental samples including industrial wastes, sludges and sediments, the method of standard additions is used.

Flameless atomization (high-temperature furnaces) has been shown by many investigators to be a reliable, highly sensitive analytical technique when proper analytical quality control procedures are practiced. In many analyses the method of standard additions is mandatory with furnace techniques to ensure valid data. Because it is basically an atomic absorption procedure, it is by definition an EPA-approved method. Therefore, application as an alternate test procedure is not required.

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TABLE VII

Results of Sample Analyses and Recovery Data for Selenium

Sample Type	No. of Samples Analyzed	No. of Positive Occurrences	Amount Detected	Technique of Determination	Spikes Analyzed No.	Spikes Analyzed Conc.	Average Recovery of Spike	Range of Spike Recoveries	Notes
Tap water	2	0	N.D. <2 µg/l	S1	2	10 µg/l	98%	96-100%	
Surface water	2	0	N.D. <2 µg/l	M1	1	20 µg/l	94%	—	Concentrated to 5x-matrix interference
Well water (N. Mexico)	6	1	5 µg/l	S1	5	4 µg/l	99%	92-109%	Other 5 samples N.D. <1 µg/l 100-µl injections
Well water (N. Mexico)	4	0	N.D. <0.5 µg/l	M1	1	5 µg/l	105%	—	Concentrated to 5x — 50 µl used for injection
Drinking water for animal exposure studies	4	4	57 µg/l 58 µg/l 59 µg/l 61 µg/l	S1	2	25 µg/l	102%	100-104%	
Sewage plant effluent	2	0	N.D. <2 µg/l	S1	1	20 µg/l	99%	—	
Industrial waste effluent	6	0	N.D. <5 µg/l	M1	5	50 µg/l	107%	104-112%	*
	3	0	N.D. <4 µg/l	S1	3	50 µg/l	97%	94-100%	Analyzed as a 1:1 dilution
Landfill leachate	1	0	N.D. <10 µg/l	M2	1	20 µg/l	92%	—	
	1	1	50 µg/l	M2	1	—	—	—	
Ocean disposal	1	0	N.D. <0.5 mg/l	S2	1	20 µg/l	88%	—	Dilution necessary—sample contained 10% SO_4
Sludges	2	0	N.D. <5 µg/g	M2	2	50 µg/l	101%	100-102%	
Sediments	3	0	N.D. <5 µg/g	M2	3	50 µg/l	98%	96-100%	
Solid gelatin ref. std.	1	1	39 µg/g	S1	Reported to contain 40 mg/l		98%		Eastman Kodak TEG-50A

S1 — standard curve 0.1% Ni matrix
S2 — standard curve 1% Ni matrix
M1 — method of standard additions in 0.1% Ni matrix
M2 — method of standard additions in 1% Ni matrix

*The concentration of the spike added to the concentration of the highest standard of addition used gave for the 25-µl injection aliquot a signal response which exceeded slightly the linearity of the curve giving erroneously high recoveries.