EPA

Source Characterization For Sewage Sludge Incinerators

Final Emissions Report
Volume III of III
Appendix K - Appendix P

Metropolitan Sewer District (MSD)
Mill Creek Wastewater Treatment Plant
Cincinnati, Ohio
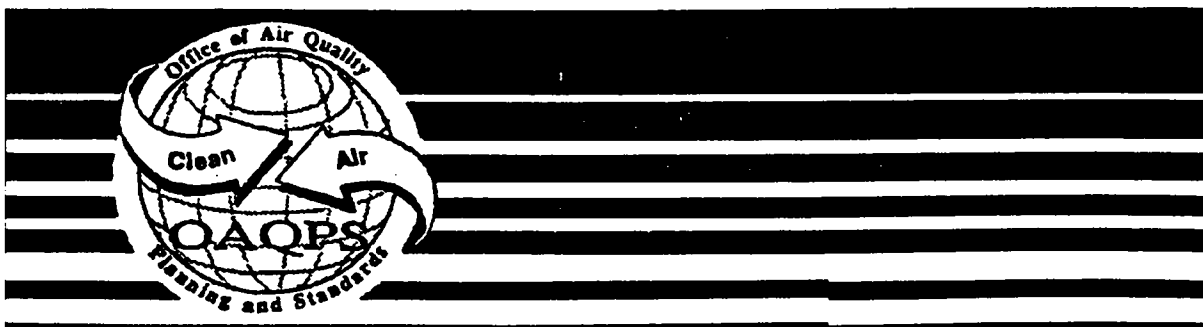
SOURCE CHARACTERIZATION FOR SEWAGE SLUDGE INCINERATORS

FINAL EMISSIONS REPORT, VOLUME III OF III, APPENDIX K - APPENDIX P

METROPOLITAN SEWER DISTRICT (MSD)
MILL CREEK WASTERWATER TREATMENT PLANT
CINCINNATI, OHIO

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U.S. ENVIRONMENTAL PROTECTION AGENCY
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APPENDIX K-1
STACK SAMPLING REFERENCE METHODS
EPA METHODS 2-5 EXAMPLE CALCULATIONS (English Units)

1. Metered Gas Sample Volume at Standard Conditions

$$V_{m(std)} = V_m \times \gamma \times \frac{528}{29.92} \times \left[\frac{P_B + \frac{\Delta H}{13.6}}{T_m + 460} \right]$$

2. Gas Volume of Water Vapor Collected in Impinger Liquid

$$V_{wc(std)} = (v_f - v_i) \times 0.04707$$

3. Gas Volume of Water Vapor Collected in Silica Gel

$$V_{wsg(std)} = (w_f - w_i) \times 0.04715$$

4. Moisture Volume Fraction in Flue Gas

$$B_{ws} = \frac{V_{wc(std)} + V_{wsg(std)}}{V_{wc(std)} + V_{wsg(std)} + V_{m(std)}}$$

5. Moisture Volume Percentage in Flue Gas

$$\%H_2O = B_{ws} \times 100$$

6. Absolute Pressure of Flue Gas

$$P_s = P_B + \frac{P_{static}}{13.6}$$

7. Nitrogen Content of Flue Gas

$$\%N_2 = 100 - (\%CO_2 + \%O_2 + \%CO)$$

8. Dry Molecular Weight of Flue Gas

$$M_d = 0.44 \times \%CO_2 + 0.32 \times \%O_2 + 0.28 \times (\%N_2 + \%CO)$$

9. Wet Molecular Weight of Flue Gas

$$M_s = M_d \times (1 - B_{ws}) + 18 \times B_{ws}$$

EPA METHODS 2-5 EXAMPLE CALCULATIONS - continued

10. Concentration at 7% O_2

$$C_{7_i} = C_i \times \frac{20.9 - 7.0}{20.9 - \%O_2}$$

11. Average Gas Velocity, ft/sec

$$v_s = 85.49 \times C_p \times (\Delta P^{1/2})_{avg} \times \frac{(T_s + 460)^{1/2}}{(P_s \times M_s)^{1/2}}$$

12. Area of Round Duct or Stack

$$A_s = \frac{\pi \times D^2}{4 \times 144} \quad \text{(round ducts)}$$

13. Actual Volumetric Flow Rate of Flue Gas

$$Q_a = v_s \times A_s \times 60$$

14. Flow Rate of Flue Gas at Standard Temperature and Pressure

$$Q_s = Q_a \times \left[\frac{P_s \times 528}{(T_s + 460) \times 29.92} \right]$$

15. Dry Flow Rate of Flue Gas at Std. Temperature and Pressure

$$Q_{sd} = Q_s \times (1 - B_{ws})$$

16. Isokinetic Variation

$$\%I = 0.09450 \times \frac{T_s V_{m(std)}}{P_s v_s A_n O (1 - B_{ws})}$$

NOMENCLATURE FOR EPA METHODS 2-5 EXAMPLE CALCS

A_s	=	Stack area, ft^2
A_n	=	Cross-sectional area of nozzle, ft^2
B_{ws}	=	Moisture volume fraction
C_p	=	Pitot tube coefficient (≈ 0.84)
C_i	=	Stack gas concentration, as measured, in ng/dscm
C_7	=	Stack gas concentration, adjusted to 7% oxygen, in ng/dscm
D_s	=	Stack diameter, inches
ΔH	=	Average meter orifice pressure, in.W.C.
ΔP	=	Pitot tube differential pressure, in.W.C.
F_c	=	Combustion factor
γ	=	Meter calibration factor, gamma
%I	=	Isokinetic Variation, percentage
L	=	Length of rectangular stack or duct, inches
M_D	=	Dry molecular weight, lb/lb-mole
M_s	=	Wet molecular weight, lb/lb-mole
P_B	=	Barometric pressure, in.Hg
P_s	=	Absolute stack pressure, in.Hg
P_{static}	=	Average static pressure, in.W.C.
Q_a	=	Actual gas flow rate, acfm
Q_s	=	Standard gas flow rate, scfm
Q_{sd}	=	Dry standard gas flow rate, dscfm
T_m	=	Average meter temperature, °F
T_s	=	Average stack temperature, °F
v_f	=	Final impinger volume, ml
v_i	=	Initial impinger volume, ml
V_m	=	Uncorrected metered gas volume, dcf
$V_{m(std)}$	=	Corrected gas volume, dscf
v_s	=	Average gas velocity, ft/sec
$V_{wc(std)}$	=	Gas volume of water caught in impingers, scf
$V_{wsg(std)}$	=	Gas volume of water caught in silica gel, scf
W	=	Width of rectangular stack or duct, inches
w_f	=	Final silica gel mass, grams
w_i	=	Initial silica gel mass, grams
$\%O_2$	=	Dry volumetric concentration of O_2, %dv
$\%CO_2$	=	Dry volumetric concentration of CO_2, %dv
$\%CO$	=	Dry volumetric concentration of CO, %dv
$\%N_2$	=	Dry volumetric concentration of N_2, %dv
%EA	=	Percent excess air
θ	=	Total sampling time, minutes

K FACTOR FOR ISOKINETIC SAMPLING

$$K = 846.72 \times D_n^4 \times \Delta H_a \times C_P^2 \times (1 - B_{ws})^2 \times \left[\frac{M_d \times (T_m + 460) \times P_s}{M_s \times (T_s + 460) \times P_m} \right]$$

NOMENCLATURE

D_n	=	Nozzle Diameter, inches
ΔH_a	=	Orifice Meter Coefficient, in. W.C.
C_p	=	Pitot tube coefficient (≈ 0.84)
B_{ws}	=	Moisture volume fraction
M_d	=	Dry molecular weight, lb/lb-mole
T_m	=	Average meter temperature, °F
M_s	=	Wet molecular weight, lb/lb-mole
P_s	=	Absolute stack pressure, in.Hg
M_s	=	Wet molecular weight, lb/lb-mole
T_s	=	Average stack temperature, °F
P_m	=	Meter Absolute Pressure, in.Hg
		(Assume $P_m = P_B$, the barometric pressure)

K-2
Example Calculations for PCB Analysis

APPENDIX K-2
EXAMPLE CALCULATIONS FOR PCB ANALYSIS

1. Concentration of the PCB compounds in the air sample.

$$C_x = \frac{A_x \times Q_{is}}{A_{is} \times \overline{RF}_n \times W_s}$$

where:

C_x	=	*concentration of unlabeled PCB congeners in the front half or back half extract (pg/dscm),*
A_x	=	*sum of the integrated ion abundances of the quantitation ions for unlabeled PCBs,* ·
A_{is}	=	*sum of the integrated ion abundances of the quantitation ions for the labeled internal standards,*
Q_{is}	=	*quantity, in pg, of the internal standard added to the sample before extraction,*
$\overline{RF}_n$	=	*calculated mean relative response factor for the analyte,*
W_s	=	*volume of air sampled (dscm).*

2. Concentration of a native PCB analyte in an emission sample is computed by summing the concentration of the front half and the back half, as follows:

$$\text{Concentration in emission sample (pg/dscm)} = C_{fh} + C_{bh}$$

where:

C_{fh} = *Concentration of the compound in the front half (pg/dscm), calculated per Equation 1.*
C_{bh} = *Concentration of the compound in the back half (pg/dscm), calculated per Equation 1.*

3. Concentration of the PCB compounds in the sludge extract

$$C_x = \frac{A_x \times Q_{is}}{A_{is} \times \overline{RF}_n \times W_s}$$

where:

C_x	=	*concentration of unlabeled PCB congeners in the sample (pg/g, dry weight),*
A_x	=	*sum of the integrated ion abundances of the quantitation ions for unlabeled PCBs,*
A_{is}	=	*sum of the integrated ion abundances of the quantitation ions for the labeled internal standards,*
Q_{is}	=	*quantity, in pg, of the internal standard added to the sample before extraction,*
$\overline{RF}_n$	=	*calculated mean relative response factor for the analyte,*
W_s	=	*weight of sample extracted (g, dry weight),*

4. Concentration of the PCB compounds in the scrubber water extract

$$C_x = \frac{A_x \times Q_{is}}{A_{is} \times \overline{RF}_n \times V_s}$$

where:

C_x	=	*concentration of unlabeled PCB congeners in the sample (pg/L),*
A_x	=	*sum of the integrated ion abundances of the quantitation ions for unlabeled PCBs,*
A_{is}	=	*sum of the integrated ion abundances of the quantitation ions for the labeled internal standards,*
Q_{is}	=	*quantity, in pg, of the internal standard added to the sample before extraction,*
$\overline{RF}_n$	=	*calculated mean relative response factor for the analyte,*
V_s	=	*volume of sample extracted (L).*

5. Calculate the percent recovery of the internal standards measured in the sample extract, using the formula:

$$Percent\ recovery = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs} \times \overline{RF}_{is}} \times 100$$

where:

A_{is}	=	*sum of the integrated ion abundances of the quantitation ions for the labeled internal standard,*
A_{rs}	=	*sum of the integrated ion abundances of the quantitation ions for the labeled recovery standard,*
Q_{is}	=	*quantity, in pg, of the internal standard added to the sample before extraction,*
Q_{rs}	=	*quantity, in pg, of the recovery standard added to the cleaned-up sample residue before HRGC/HRMS analysis, and*
$\overline{RF}_{is}$	=	*calculated mean relative response factor for the labeled internal standard relative to the appropriate recovery standard.*

Calculate the percent recovery of the cleanup standard similarly.

6. Accuracy

Accuracy is defined as the agreement between a measurement and the actual (i.e., true) value. Accuracy is expressed as the percent recovery of an analyte that has been used to fortify an investigative sample (XAD resin) or a standard matrix (e.g., analyte free water) at a known concentration prior to analysis, and is expressed by the following formula:

$$Accuracy = \% \, Recovery = \frac{A_T - A_O}{A_F} \, x \, 100$$

where:

A_t	=	Total amount found in fortified sample or standard
A_o	=	Amount found in unfortified sample
A_F	=	Amount added to sample.

Laboratory accuracy will be assessed through the analysis of matrix spikes and surrogate spikes and the determination of percent recoveries.

7.   Precision

Precision is defined in *EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations*, U.S. EPA QA/R-5, as the measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions expressed generally in terms of analysis of samples relative to the average of those results for a given analyte using the formula:

$$\% RSD = \frac{\sigma}{X} \, x \, 100$$

where:

%RSD	=	Relative standard deviation
σ	=	Standard deviation of the triplicate sample results
X	=	Average of the triplicate results.

8.   Completeness

Completeness is a measure of the relative number of analytical data points that meet all of the acceptance criteria for accuracy, precision, and any other criteria required by the specific analytical methods used. The level of completeness can also be affected by loss or breakage of samples during transport, as well as external problems that prohibit collection of the sample.

K-3
Relative Standard Deviation Calculation Worksheet

PCB Congener	Air Table 2-2 R2	R3	R4	Air Mean	SD	%RSD	WI R4	Water Table 2-12 WI R2	WI R3	Water In Mean	SD	%RSD
3,3',4,4'-tetrachlorobiphenyl (TCB) (PCB-77)	25.130	21.696	7.151	17.992	9.545	53.048	0.21	0.156	0.166	0.178	0.028	15.730
2,3,4,4'-pentachlorobiphenyl (PeCB) (PCB-105)	2.669	2.455	0.945	2.023	0.940	46.450	1.909	0.89	0.491	1.030	0.768	74.535
2,3,4',5-pentachlorobiphenyl (PeCB) (PCB-114)	0.389	0.340	0.137	0.289	0.134	46.286	0.245	0.233	0.068	0.182	0.099	54.346
2,3',4,4',5-pentachlorobiphenyl (PeCB) (PCB-118)	5.721	5.268	2.211	4.400	1.909	43.391	3.847	1.201	1.065	2.038	1.568	76.971
2',3,4,4',5-pentachlorobiphenyl (PeCB) (PCB-123)	0.120	0.112	0.036	0.090	0.045	50.234	0.109	0.177	0.032	0.106	0.073	68.440
3,3',4,4',5-pentachlorobiphenyl (PeCB) (PCB-126)	0.700	0.584	0.211	0.398	0.264	66.352 ND		0.024	0.007	0.016	0.012	77.554
2,3,3',4,4',5-hexachlorobiphenyl (HxCB) (PCB-156)#	0.645	0.565	0.356	0.522	0.149	28.586	0.227	0.243	0.085	0.185	0.087	47.011
2,3,3',4,4',5'-hexachlorobiphenyl (HxCB) (PCB-157)#	0.221	0.179	0.079	0.160	0.073	45.687	0.081	0.166	0.265	0.177	0.102	57.784
2,3',4,4',5,5'-hexachlorobiphenyl (HxCB) (PCB-167)	0.388	0.337	0.136	0.287	0.133	46.423	0.126	0.166	0.044	0.119	0.071	60.070
3,3',4,4',5,5'-hexachlorobiphenyl (HxCB) (PCB-169)	0.560	0.467	0.140	0.389	0.221	56.709	0.009	0.027	0.006	0.014	0.011	81.127
2,2',3,3',4,4',5-heptachlorobiphenyl (HpCB) (PCB-170)	1.081	0.966	0.437	0.828	0.343	41.481	0.166	0.105	0.08	0.117	0.044	37.810
2,2',3,4,4',5,5'-heptachlorobiphenyl (HpCB) (PCB-180)	2.690	2.374	0.856	1.973	0.980	49.685	0.37	0.338	0.19	0.299	0.096	32.081
2,3,3',4,4',5,5'-heptachlorobiphenyl (HpCB) (PCB-189)	0.095	0.076	0.044	0.072	0.026	35.965	0.013	0.029	0.009	0.017	0.011	62.253

D/F	Air Table 2-6 R2	R3	R4	Air Mean	SD	%RSD	Scrubber Water Inlet WI R2	WI R3	WI R4	Water In Mean	SD	%RSD
2,3,7,8-TCDD #	0.098	0.067	0.034	0.066	0.032	48.249	ND	ND	ND	#VALUE!	#DIV/0!	#DIV/0!
Total TCDD	3.024	3.534	0.719	2.426	1.500	61.833	ND	0.002	ND	0.002	#DIV/0!	#DIV/0!
1,2,3,7,8-PCDD	0.017	0.013	0.005	0.012	0.006	52.372	ND	ND	ND			
Total PCDD	0.706	0.658	0.186	0.517	0.286	55.326	ND	ND	ND			
1,2,3,4,7,8-HxCDD	0.015	0.015	0.006	0.012	0.005	43.301	ND	ND	ND			
1,2,3,6,7,8-HxCDD	0.038	0.039	0.013	0.030	0.015	49.103	ND	ND	ND			
1,2,3,7,8,9-HxCDD	0.039	0.035	0.016	0.030	0.012	40.961	ND	ND	ND			
Total HxCDD	0.606	0.583	0.324	0.504	0.157	31.050	ND	ND	ND			
1,2,3,4,6,7,8-HpCDD	0.204	0.203	0.093	0.167	0.064	38.279	ND	ND	ND			
Total HpCDD	0.459	1.453	0.237	0.716	0.648	90.398	ND	ND	ND			
Octa CDD	0.317	0.303	0.14	0.253	0.098	38.842	0.04	0.012	0.016	0.023	0.015	66.811
Total CDD	5.113	6.469	1.608	4.397	2.508	57.053	0.04	0.013	0.016	0.023	0.015	64.342
2,3,7,8-TCDF #	1.583	1.237	0.533	1.118	0.535	47.874	ND	ND	ND			
Total TCDF	5.607	4.879	2.571	4.352	1.585	36.418	ND	0.002	ND	0.002	#DIV/0!	#DIV/0!
1,2,3,7,8-PCDF	0.195	0.15	0.067	0.137	0.065	47.282	ND	ND	ND			
2,3,4,7,8-PCDF	0.389	0.282	0.123	0.265	0.134	50.571	ND	ND	ND			
Total PCDF	4.933	3.666	1.536	3.378	1.717	50.814	ND	ND	ND			
1,2,3,4,7,8-HxCDF	0.226	0.178	0.091	0.165	0.068	41.474	ND	ND	ND			
1,2,3,6,7,8-HxCDF	0.081	0.066	0.035	0.061	0.023	38.669	ND	ND	ND			
2,3,4,6,7,8-HxCDF	0.126	0.097	0.051	0.091	0.038	41.408	ND	ND	ND			
1,2,3,7,8,9-HxCDF	ND	ND	ND	ND	ND	#VALUE!	ND	ND	ND			
Total HxCDF	1.126	0.880	0.41	0.805	0.364	45.173	ND	ND	ND			
1,2,3,4,6,7,8-HpCDF	0.223	0.184	0.102	0.170	0.062	38.401	ND	0.001	ND			
1,2,3,4,7,8,9-HpCDF	0.022	0.017	0.009	0.016	0.007	40.984	ND	ND	ND			
Total HpCDF	0.328	0.261	0.136	0.242	0.097	40.324	ND	0.004	0.003	0.004	0.001	20.203
Octa CDF	0.09	0.083	0.042	0.072	0.026	36.181	ND	ND	ND			
Total CDF	12.084	9.768	4.697	8.850	3.778	42.693	0.092	0.005	0.003	0.033	0.051	152.450
Total CDD + CDF	17.197	16.237	6.305	13.246	8.031	45.526	0.132	0.002	0.019	0.051	0.071	138.551

Water

WO R2	WO R3	WO R4	Mean	SD	Water Out %RSD	Sludge S R2	S R3	S R4	Mean	SD	Sludge %RSD	PCB Congener
4.185	1.837	2.52	2.847	1.20774	42.417	40.899	41.096	45.386	42.460	2.535618	5.972	3,3',4,4'-tetrachlorobiphenyl (TCB) (PCB-77)
0.946	0.642	0.854	0.814	0.155897	19.152	7.015	7.389	7.289	7.231	0.193829	2.678	2,3,3',4,4'-pentachlorobiphenyl (PeCB) (PCB-105)
0.157	0.074	0.124	0.118	0.041789	35.315	0.691	0.674	0.738	0.701	0.033151	4.729	2,3,4,4',5-pentachlorobiphenyl (PeCB) (PCB-114)
1.676	1.272	1.621	1.523	0.219105	14.386	12.25	13.497	12.856	12.868	0.623582	4.846	2,3',4,4',5-pentachlorobiphenyl (PeCB) (PCB-118)
0.066	0.022	0.05	0.053	0.032083	60.916	0.231	0.276	0.241	0.249	0.023629	9.477	2',3,4,4',5-pentachlorobiphenyl (PeCB) (PCB-123)
0.135	0.048	0.096	0.093	0.04471	48.075	1.118	1.214	1.479	1.270	0.186977	14.719	3,3',4,4',5-pentachlorobiphenyl (PeCB) (PCB-126)
0.249	0.116	0.236	0.200	0.073323	36.661	1.772	1.883	1.876	1.844	0.062164	3.372	2,3,3',4,4',5-hexachlorobiphenyl (HxCB) (PCB-156)#
0.119	0.033	0.083	0.078	0.04319	55.136	0.472	0.565	0.536	0.524	0.047585	9.075	2,3,3',4,4',5'-hexachlorobiphenyl (HxCB) (PCB-157)#
0.156	0.06	0.125	0.114	0.049663	43.612	0.878	0.968	0.959	0.935	0.049568	5.301	2,3',4,4',5,5'-hexachlorobiphenyl (HxCB) (PCB-167)
0.113	0.048	0.096	0.086	0.034034	39.422	0.453	0.601	0.656	0.570	0.10499	18.419	3,3',4,4',5,5'-hexachlorobiphenyl (HxCB) (PCB-169)
0.264	0.143	0.298	0.235	0.061468	34.647	2.526	2.572	2.776	2.625	0.133061	5.870	2,2',3,3',4,4',5-heptachlorobiphenyl (HpCB) (PCB-170)
0.666	0.366	0.653	0.568	0.176001	30.968	6.002	6.76	6.711	6.498	0.430644	6.628	2,2',3,4,4',5,5'-heptachlorobiphenyl (HpCB) (PCB-180)
0.03	0.014	0.044	0.029	0.015011	51.174	0.181	0.198	0.218	0.199	0.01852	9.307	2,3,3',4,4',5,5'-heptachlorobiphenyl (HpCB) (PCB-189)

Scrubber Water Outlet

WO R2	WO R3	WO R4	Mean	SD	Water Out %RSD	Sludge S R2	S R3	S R4	Mean	SD	Sludge %RSD	D/F
0.009	0.013	0.014	0.012	0.003	22.048	ND	ND	ND	NA	NA	#VALUE!	2,3,7,8-TCDD #
0.475	0.621	0.277	0.524	0.275	52.511	0.068	0.063	0.095	0.082	0.014	16.497	Total TCDD
ND	ND	ND	NA	NA	#VALUE!	ND	ND	ND	NA	NA	#VALUE!	1,2,3,7,8-PCDD
0.046	0.057	(0.066)	#VALUE!	0.008	#VALUE!	0.03	0.023	0.03	0.028	0.004	14.608	Total PCDD
0.002	ND	0.003	0.003	0.001	28.264	ND	ND	0.008	0.006	#DIV/0!	#DIV/0!	1,2,3,4,7,8-HxCDD
0.003	ND	0.006	0.005	0.002	47.146	0.015	0.018	0.031	0.021	0.009	39.867	1,2,3,6,7,8-HxCDD
(0.003)	ND	0.006	#VALUE!	#DIV/0!	#DIV/0!	0.027	0.024	0.04	0.030	0.009	28.038	1,2,3,7,8,9-HxCDD
(0.029)	0.054	0.102	#VALUE!	0.034	#VALUE!	0.128	0.135	0.02	0.094	0.064	68.342	Total HxCDD
(0.011)	0.025	0.032	#VALUE!	0.005	#VALUE!	0.229	0.261	0.384	0.298	0.079	26.472	1,2,3,4,6,7,8-HpCDD
0.027	0.053	0.074	0.051	0.024	45.865	0.431	0.52	0.702	0.551	0.138	25.070	Total HpCDD
0.03	0.059	0.047	0.045	0.015	32.143	2.51	2.688	3.689	2.962	0.636	21.455	Octa CDD
0.806	1.043	0.565	0.739	0.264	35.799	3.167	3.449	4.533	3.716	0.721	19.405	Total CDD
0.181	0.222	0.256	0.220	0.038	17.096	0.028	0.03	0.039	0.032	0.006	18.122	2,3,7,8-TCDF #
0.824	1.12	0.666	0.937	0.160	17.098	0.078	0.096	0.12	0.097	0.022	22.634	Total TCDF
0.014	0.025	0.025	0.021	0.006	29.770	ND	ND	0.013	0.013	#DIV/0!	#DIV/0!	1,2,3,7,8-PCDF
0.029	0.045	0.053	0.042	0.012	28.867	0.006	0.009	0.013	0.010	0.003	26.458	2,3,4,7,8-PCDF
0.316	0.493	0.495	0.435	0.103	23.644	0.03	0.095	0.163	0.096	0.067	69.277	Total PCDF
0.012	0.016	0.025	0.018	0.007	37.689	0.014	0.019	0.03	0.021	0.008	38.978	1,2,3,4,7,8-HxCDF
0.005	0.007	0.011	0.008	0.003	39.848	ND	0.006	0.01	0.008	0.003	35.355	1,2,3,6,7,8-HxCDF
(0.006)	0.013	0.017	#VALUE!	0.003	#VALUE!	0.006	0.008	0.013	0.009	0.004	40.062	2,3,4,6,7,8-HxCDF
ND	ND	ND	NA	NA	#VALUE!	ND	ND	ND	NA	NA	#VALUE!	1,2,3,7,8,9-HxCDF
0.048	0.08	0.113	0.080	0.033	40.458	0.098	0.117	0.171	0.129	0.038	29.435	Total HxCDF
0.012	0.02	0.025	0.019	0.007	34.513	0.132	0.159	0.222	0.171	0.046	27.008	1,2,3,4,6,7,8-HpCDF
ND	ND	ND	NA	NA	#VALUE!	ND	ND	ND	NA	NA	#VALUE!	1,2,3,7,8,9-HpCDF
0.017	0.028	(0.035)	#VALUE!	0.008	#VALUE!	0.239	0.284	0.377	0.300	0.070	23.450	Total HpCDF
0.006	10.396	0.008	3.470	5.996	172.856	0.313	0.34	0.441	0.365	0.067	18.502	Octa CDF
1.121	1.733	1.416	1.424	0.306	21.492	0.756	0.932	1.272	0.987	0.262	26.585	Total CDF
1.819	2.776	1.983	2.193	0.512	23.341	3.923	4.381	5.805	4.703	0.981	20.869	Total CDD + CDF

K-12

K-4
Gas Concentration Correction to
7% O$_2$ Worksheet

9/3/99

Air Cor   · 7% Oxygen
Dioxin/Furan Results
MSD Incinerator Test
Cincinnati, OH

WA1-05
Draft Test Report

Analyte	Uncorrected Concentration		ng/dscm		Corrected Concentration		ng/dscm
	Run 2	Run 3	Run 4		Run 2	Run 3	Run 4
Dioxins							
2,3,7,8-TCDD #	0.107	0.067	0.034		0.209	0.118	0.063
Total TCDD	3.025	3.534	0.719		5.922	6.218	1.333
1,2,3,7,8-PCDD	0.017	0.013	0.005		0.033	0.023	0.009
Total PCDD	0.706	0.658	0.188		1.382	1.158	0.348
1,2,3,4,7,8-HxCDD	0.015	0.015	0.006		0.029	0.026	0.011
1,2,3,6,7,8-HxCDD	0.038	0.039	0.013		0.074	0.069	0.024
1,2,3,7,8,9-HxCDD	0.039	0.035	0.016		0.076	0.062	0.030
Total HxCDD	0.606	0.583	0.324		1.186	1.026	0.600
1,2,3,4,6,7,8-HpCDD	0.204	0.203	0.093		0.399	0.357	0.172
Total HpCDD	0.459	1.453	0.237		0.899	2.557	0.439
Octa CDD	0.317	0.241	0.14		0.621	0.424	0.259
Total CDD	5.113	6.469	1.608		10.010	11.382	2.980
Furans							
2,3,7,8-TCDF #	1.583	1.236	0.533		3.099	2.175	0.988
Total TCDF	5.607	4.879	2.571		10.977	8.585	4.765
1,2,3,7,8-PCDF	0.195	0.15	0.067		0.382	0.264	0.124
2,3,4,7,8-PCDF	0.389	0.282	0.123		0.762	0.496	0.228
Total PCDF	4.933	3.666	1.536		9.658	6.450	2.847
1,2,3,4,7,8-HxCDF	0.226	0.178	0.091		0.442	0.313	0.169
1,2,3,6,7,8-HxCDF	0.081	0.066	0.035		0.159	0.116	0.065
2,3,4,6,7,8-HxCDF	0.126	0.097	0.051		0.247	0.171	0.095
1,2,3,7,8,9-HxCDF	ND	ND	ND		ND	ND	ND
Total HxCDF	1.126	0.879	0.41		2.204	1.547	0.760
1,2,3,4,6,7,8-HpCDF	0.223	0.184	0.102		0.437	0.324	0.189
1,2,3,4,7,8,9-HpCDF	0.022	0.017	0.009		0.043	0.030	0.017
Total HpCDF	0.328	0.261	0.136		0.642	0.459	0.252
Octa CDF	0.09	0.083	0.042		0.176	0.146	0.078
Total CDF	12.084	9.768	4.697		23.657	17.187	8.705
Total CDD + CDF	17.197	16.237	6.305		33.667	28.569	11.685

O_2 Concentration   R2 Formula: Uncorrected * 13.9/7.1
Correction Eqn.   R3 Formula: Uncorrected * 13.9/7.9
                      R4 Formula: Uncorrected * 13.9/7.5

9/24/99

Air Correction ... ..xygen
PCB Results
MSD Incinerator Test
Cincinnati, OH

WA 1-05
Revised Draft Test Report

	Uncorrected Concentration		ng/dscm	7% O_2 Corrected Concentration			ng/dscm	TEFs	WHO Toxic Equivalent Corrected Concentration			ng/dscm
Analyte	Run 2	Run 3	Run 4	Run 2	Run 3	Run 4			Run 2	Run 3	Run 4	
PCB-77	15.623	10.681	4.275	30.586	18.793	7.923	1.00E-04		3.06E-03	1.88E-03	7.92E-04	
PCB-105	2.669	2.455	0.945	5.225	4.320	1.751	1.00E-04		5.23E-04	4.32E-04	1.75E-04	
PCB-114	0.389	0.340	0.137	0.762	0.598	0.254	5.00E-04		3.81E-04	2.99E-04	1.27E-04	
PCB-118	5.722	5.268	2.211	11.202	9.269	4.098	1.00E-04		1.12E-03	9.27E-04	4.10E-04	
PCB-123	0.121	0.111	0.038	0.237	0.195	0.070	1.00E-04		2.37E-05	1.95E-05	7.04E-06	
PCB-126	0.700	0.584	0.210	1.370	1.028	0.389	0.1		1.37E-01	1.03E-01	3.89E-02	
PCB-156	0.645	0.565	0.213	1.263	0.994	0.395	5.00E-04		6.31E-04	4.97E-04	1.97E-04	
PCB-157	0.221	0.179	0.079	0.433	0.315	0.146	5.00E-04		2.16E-04	1.57E-04	7.32E-05	
PCB-167	0.388	0.337	0.136	0.760	0.593	0.252	1.00E-05		7.60E-06	5.93E-06	2.52E-06	
PCB-169	0.559	0.467	0.141	1.094	0.822	0.261	0.01		1.09E-02	8.22E-03	2.61E-03	
PCB-170	1.080	0.966	0.437	2.114	1.700	0.810	1.00E-04		2.11E-04	1.70E-04	8.10E-05	
PCB-180	2.689	2.374	0.856	5.264	4.177	1.586	1.00E-05		5.26E-05	4.18E-05	1.59E-05	
PCB-189	0.095	0.076	0.044	0.186	0.134	0.082	1.00E-04		1.86E-05	1.34E-05	8.15E-06	

K-15

O_2 Concentration R2 Formula: Uncorrected * 13.9/7.1
Correction Eqn.   R3 Formula: Uncorrected * 13.9/7.9
   R4 Formula: Uncorrected * 13.9/7.5

Corrected * TEF = TEQ Concentration
Concentration

Concentration Correction to Sta____ Volume and 7% Oxygen
PAH Air Resu___
MSD Incinerator Test
Cincinnati, OH Results
MSD Incinerator Test
Cincinnati, OH

Analyte	Lab Concentration (ng/sample)			Sampled Volume (dscm)			Uncorrected Concentration			Corrected Concentration		
	Run 2	Run 3	Run 4	Run 2	Run 3	Run 4	Run 2	Run 3	Run 4	Run 2	Run 3	Run 4
PAHs												
Acenaphthene	160	130	26	1.462	1.555	1.675	109.4391	83.60129	15.52239	214.2541	147.0959	28.76816
Acenaphthylene	1700	2000	260	1.462	1.555	1.675	1162.791	1286.174	155.2239	2276.449	2263.014	287.6816
Anthracene	210	82	93	1.462	1.555	1.675	143.6389	52.73312	55.52239	281.2085	92.78359	102.9015
Benzo(a)anthracene	136	390	82	1.462	1.555	1.675	93.02326	250.8039	48.95522	182.116	441.2878	90.73035
Benzo(b)fluoranthene	1210	1030	266	1.462	1.555	1.675	827.6334	662.3794	158.806	1620.296	1165.452	294.3204
Benzo(k)fluoranthene	1110	562	157	1.462	1.555	1.675	759.2339	361.4148	93.73134	1486.388	835.907	173.7154
Benzo(g,h,i)perylene	340	209	85	1.462	1.555	1.675	232.5581	134.4051	50.74627	455.2699	238.485	94.04975
Benzo(a)pyrene	110	53	0	1.462	1.555	1.675	75.2394	34.0836	0	147.2997	59.96988	0
Benzo(e)pyrene	9200	10340	270	1.462	1.555	1.675	6292.75	6649.518	161.194	12319.61	11699.78	298.7463
Chrysene	3500	2077	483	1.462	1.555	1.675	2393.981	1335.691	288.3582	4686.806	2350.14	534.4239
Dibenzo(a,h)anthracene	105	76	21	1.462	1.555	1.675	71.81943	48.8746	12.53731	140.6042	85.99455	23.23582
Fluoranthene	3953	3633	933	1.462	1.555	1.675	2703.83	2336.334	557.0149	5293.414	4110.786	1032.334
Fluorene	1500	1700	130	1.462	1.555	1.675	1025.992	1093.248	77.61194	2008.632	1923.582	143.8408
Indeno(1,2,3-c,d)pyrene	357	258	74	1.462	1.555	1.675	244.186	165.9164	44.1791	478.0544	291.9289	81.87861
2-Methylnaphthalene	32040	30037	1327	1.462	1.555	1.675	21915.18	19316.4	792.2388	42904.38	33987.08	1468.283
Naphthalene	451700	380530	210440	1.462	1.555	1.675	308960.3	244713.8	125635.8	604866	430572.4	232845.1
Perylene	370	0	57	1.462	1.555	1.675	253.078	0	34.02985	495.4625	0	63.06866
Pyrene	2643	2427	490	1.462	1.555	1.675	1807.798	1560.772	292.5373	3539.209	2746.168	542.1692
Phenanthrene	33130	33000	8000	1.462	1.555	1.675	22660.74	21221.86	4776.119	44363.98	37339.74	8851.741

Uncorrected Concentration = Lab Conc. (ng/sample) / Sample aliquot volume (dscm)
(dry, std conditions)

O_2 Concentration Correction Eqn.

R2 Formula: Uncorrected * 13.9/7.1
R3 Formula: Uncorrected * 13.9/7.9
R4 Formula: Uncorrected * 13.9/7.5

APPENDIX L

Continuous Emissions Monitoring (CEM) Data

L-1
CEM Test Data Summary

Table L-1. CEM Daily Results

CEM	Daily Test Run Averages			
	Run 2	Run 3	Run 4	Average
CO^*, ppm_{dv}	1380	1170	1130	1230
THC^b, ppm_{dv}	70.6	54.2	37.5	54.1
CO_2^*, % v	5.16	5.50	5.07	5.24
O_2^*, % v	13.7	13.0	13.4	13.4

[*] CO, CO_2, and O_2 analyzer data calibration corrected from 1-minute averages during the 360 minute sampling run.

[b] THC analyzer data calibration corrected from the arithmetic average of hourly reported values from MSD during the sampling runs.

L-1-1
CEM Daily Results

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR
LINEARITY CHECK
JULY 19, 1999

Starting
07-19-99

Time	O2 %dv	CO2 %dv	CO ppmdv
12:21	4.07	4.82	-3.32
12:22	0.11	0.78	-3.32
12:23	0.06	0.57	-1.63
12:24	0.09Z	0.16Z	0.00Z
12:25	21.06H	17.90H	0.00
12:26	15.01	13.58	0.00
12:27	11.71M	10.93M	0.00
12:28	0.06	0.17	2129.00
12:29	0.02	0.13	3042.00
12:30	0.01	0.12	3005.00H
12:31	0.03	0.14	2953.00
12:32	0.01	0.13	1376.00
12:33	0.02	0.13	911.00L
12:34	0.15	0.22	1060.00
12:35	-0.00	0.11	1742.00
12:36	0.00	0.11	1819.00M
12:37	0.05	0.11	1820.00
12:38	0.15	0.12	1815.00
12:39	4.00	0.14	1815.00
12:40	5.97	0.15	1814.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR
LINEARITY CHECK
JULY 20, 1999

Starting
07-20-99

Time	O2 %dv	CO2 %dv	CO ppmdv
07:56	0.00	0.10	3971.00
07:57	0.00Z	0.10Z	254.00
07:58	3.25	2.20	6.07Z
07:59	21.06H	18.05H	5.73
08:00	18.96	16.35	-4.86
08:01	11.80M	10.96M	0.39
08:02	19.61	17.27	-5.65
08:03	11.98	10.98	-5.37
08:04	12.66	11.48	2.18
08:05	14.76	2.13	659.20
08:06	18.82	13.68	2568.00
08:07	21.31	17.40	126.50
08:08	11.68	11.00	-4.25
08:09	11.32	10.94	-5.03
08:10	0.32	0.52	2592.00
08:11	0.05	0.11	5890.00
08:12	0.03	0.10	4771.00
08:13	0.08	0.14	1933.00
08:14	0.03	0.10	1897.00
08:15	0.04	0.12	2097.00
08:16	0.01	0.10	3075.00
08:17	0.01	0.10	4231.00
08:18	0.01	0.10	5009.00
08:19	0.00	0.10	5799.00
08:20	0.00	0.10	5922.00H
08:21	0.00	0.09	5909.00
08:22	0.00	0.10	4343.00
08:23	0.00	0.09	1806.00
08:24	0.04	0.12	1878.00L
08:25	0.02	0.10	1756.00
08:26	0.02	0.09	2027.00
08:27	0.00	0.09	3016.00
08:28	0.26	0.15	3105.00M
08:29	7.09	0.14	2922.00
08:30	8.39	0.14	1183.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR
LINEARITY CHECK
JULY 21, 1999

Starting
07-21-99

Time	O2 %dv	CO2 %dv	CO ppmdv
09:01	8.26	0.57	1550.00
09:02	8.05	0.57	1550.00
09:03	7.20	0.56	1539.00
09:04	1.08	0.19	619.50
09:05	0.00Z	0.11Z	-0.45Z
09:06	6.23	5.23	-2.29
09:07	10.72	8.76	4.59
09:08	20.99H	18.46H	-6.60
09:09	16.69	14.45	-6.43
09:10	11.75M	11.12M	82.60
09:11	0.07	0.15	5532.00
09:12	0.08	0.13	5676.00H
09:13	0.06	0.11	2986.00
09:14	0.00	0.09	1878.00L
09:15	0.05	0.10	1808.00
09:16	-0.00	0.09	2957.00
09:17	0.00	0.09	4689.00
09:18	-0.01	0.09	5881.00
09:19	-0.01	0.09	3975.00
09:20	-0.01	0.08	1908.00
09:21	-0.01	0.08	2724.00
09:22	-0.01	0.08	3106.00M
09:23	0.06	0.10	3100.00
09:24	1.24	0.25	3040.00
09:25	0.22	0.11	1343.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR
LINEARITY CHECK
JULY 22, 1999

Starting
07-22-99

Time	O2 %dv	CO2 %dv	CO ppmdv
06:41	9.26	0.57	1571.00
06:42	1.48	0.18	870.00
06:43	0.00	0.10	75.60
06:44	0.00Z	0.11Z	3.63Z
06:45	15.16	8.26	7.16
06:46	20.81H	17.96H	1.01
06:47	20.10	17,28	-6.32
06:48	11.53L	10.91L	-5.65
06:49	6.80	6.79	105.70
06:50	0.03	0.13	4458.00
06:51	0.01	0.10	5925.00H
06:52	0.02	0.09	5894.00
06:53	0.16	0.11	3896.00
06:54	-0.00	0.09	1898.00
06:55	-0.00	0.09	1852.00L
06:56	0.11	0.09	2273.00
06:57	-0.00	0.09	3045.00M
06:58	0.06	0.09	2008.00
06:59	-0.07	0.08	474.10
07:00	8.38	3.31	394.40

Marker	Description	Display	Average
A	Data was Absent from original raw data file.	√	
C	CYLINDER GAS AUDIT	√	
D	DELAY FOR SAMPLING TRAIN TROUBLESHOOTING	√	
H	HIGH CALIBRATION GAS	√	
L	LOW CALIBRATION GAS	√	
M	MID CALIBRATION GAS	√	
P	SAMPLING POINT	√	√
R	RESPONSE TIME	√	
Z	ZERO CALIBRATION GAS	√	
*	Data was not used in calculated parameter averages.		

L-2
One Minute Data Printouts

L-2-1
Daily Data

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 2A
JULY 20, 1999

Starting
07-20-99

Time	O2 % dv	CO2 %dv	CO ppmdv
15:01	14.25	4.85	1407.00
15:02	14.25	4.85	1395.00
15:03	14.18	4.89	1389.00
15:04	14.23	4.87	1391.00
15:05	14.18	4.90	1353.00
15:06	14.18	4.89	1399.00
15:07	14.17	4.92	1403.00
15:08	14.12	4.96	1380.00
15:09	14.18	4.92	1392.00
15:10	14.23	4.89	1413.00
15:11	14.24	4.89	1438.00
15:12	14.28	4.87	1436.00
15:13	14.23	4.89	1425.00
15:14	14.24	4.88	1395.00
15:15	14.16	4.94 -	1408.00
15:16	14.13	4.97	1445.00
15:17	14.09	5.00	1429.00
15:18	14.04	5.04	1416.00
15:19	14.11	4.99	1419.00
15:20	14.14	4.96	1444.00
15:21	14.09	4.99	1435.00
15:22	14.01	5.06	1400.00
15:23	14.04	5.05	1404.00
15:24	13.98	5.10	1411.00
15:25	14.04	5.05	1378.00
15:26	13.97	5.10	1362.00
15:27	13.99	5.08	1377.00
15:28	13.94	5.11	1353.00
15:29	13.90	5.15	1370.00
15:30	13.90	5.16	1375.00
15:31	13.84	5.22	1370.00
15:32	13.88	5.17	1368.00
15:33	13.83	5.20	1364.00
15:34	13.86	5.18	1377.00
15:35	13.86	5.18	1397.00
15:36	13.89	5.15	1390.00
15:37	13.89	5.15	1425.00
15:38	13.90	5.14	1426.00
15:39	13.89	5.14	1434.00
15:40	13.87	5.17	1447.00
15:41	13.83	5.19	1461.00
15:42	13.94	5.10	1465.00
15:43	14.00	5.03	1471.00
15:44	13.99	5.05	1463.00
15:45	13.99	5.03	1444.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 2A
JULY 20, 1999

Starting
07-20-99

Time	O2 % dv	CO2 %dv	CO ppmdv
15:46	13.97	5.05	1447.00
15:47	14.06	4.98	1447.00
15:48	14.10	4.94	1462.00
15:49	14.01	5.01	1466.00
15:50	13.99	5.02	1446.00
15:51	13.97	5.04	1425.00
15:52	14.03	4.98	1470.00
15:53	14.09	4.95	1494.00
15:54	14.19	4.86	1476.00
15:55	14.10	4.93	1449.00
15:56	14.09	4.94	1403.00
15:57	13.99	5.02	1422.00
15:58	13.78	5.14	1405.00
15:59	13.66	5.23	1387.00
16:00	13.55	5.32	1407.00
16:01	13.39	5.45	1387.00
16:02	13.33	5.49	1398.00
16:03	13.30	5.50	1398.00
16:04	13.27	5.53	1426.00
16:05	13.16	5.62	1429.00
16:06	13.15	5.65	1422.00
16:07	13.22	5.60	1407.00
16:08	13.25	5.59	1371.00
16:09	13.36	5.50	1353.00
16:10	13.35	5.51	1379.00
16:11	13.36	5.50	1387.00
16:12	13.29	5.57	1403.00
16:13	13.24	5.62	1416.00
16:14	13.18	5.66	1444.00
16:15	13.29	5.58	1455.00
16:16	13.36	5.51	1456.00
16:17	13.29	5.57	1462.00
16:18	13.40	5.48	1462.00
16:19	13.36	5.53	1459.00
16:20	13.37	5.52	1465.00
16:21	13.37	5.53	1449.00
16:22	13.47	5.45	1469.00
16:23	13.43	5.48	1465.00
16:24	13.44	5.46	1453.00
16:25	13.47	5.43	1430.00
16:26	13.57	5.37	1419.00
16:27	13.61	5.33	1398.00
16:28	13.63	5.30	1394.00
16:29	13.58	5.32	1415.00
16:30	13.56	5.34	1393.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 2A
JULY 20, 1999

Starting
07-20-99

Time	O2 % dv	CO2 %dv	CO ppmdv
16:31	13.56	5.35	1376.00
16:32	13.41	5.47	1353.00
16:33	13.45	5.43	1377.00
16:34	13.50	5.41	1396.00
16:35	13.58	5.35	1398.00
16:36	13.46	5.45	1384.00
16:37	13.51	·5.40	1381.00
16:38	13.67	5.27	1392.00
16:39	13.65	5.27	1397.00
16:40	13.68	5.24	1428.00
16:41	13.77	5.16	1457.00
16:42	13.77	5.16	1457.00
16:43	13.76	5.18	1487.00
16:44	13.77	5.16	1503.00
16:45	13.76	5.17	1507.00
16:46	13.79D	5.15D	1537.00D
16:47	13.71D	5.22D	1546.00D
16:48	13.68D	5.23D	1543.00D
16:49	13.69D	5.23D	1536.00D
16:50	13.71D	5.22D	1522.00D
16:51	13.61D	5.31D	1500.00D
16:52	13.64D	5.29D	1496.00D
16:53	13.72D	5.20D	1476.00D
16:54	13.63D	5.28D	1446.00D
16:55	13.54D	5.36D	1437.00D
16:56	13.44D	5.44D	1428.00D
16:57	13.55D	5.34D	1429.00D
16:58	13.41D	5.44D	1415.00D
16:59	13.42D	5.44D	1394.00D
17:00	13.29D	5.55D	1398.00D
17:01	13.23	5.61	1373.00
17:02	13.18	5.65	1355.00
17:03	13.13	5.69	1337.00
17:04	13.21	5.62	1352.00
17:05	13.18	5.67	1341.00
17:06	13.21	5.64	1337.00
17:07	13.35	5.54	1334.00
17:08	13.46	5.44	1346.00
17:09	13.48	5.44	1337.00
17:10	13.60	5.34	1339.00
17:11	13.68	5.28	1377.00
17:12	13.74	5.23	1344.00
17:13	13.76	5.21	1360.00
17:14	13.83	5.16	1358.00
17:15	13.85	5.15	1333.00

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METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 2A
JULY 20, 1999

Starting
07-20-99

Time	O2 % dv	CO2 %dv	CO ppmdv
17:16	13.90	5.10	1309.00
17:17	13.96	5.06	1297.00
17:18	13.96	5.05	1286.00
17:19	14.05	4.97	1269.00
17:20	14.12	4.90	1269.00
17:21	14.16	4.87	1248.00
17:22	14.14	4.87	1267.00
17:23	14.18	4.83	1288.00
17:24	14.17	4.85	1299.00
17:25	14.15	4.87	1308.00
17:26	14.20	4.82	1317.00
17:27	14.26	4.76	1313.00
17:28	14.25	4.75	1334.00
17:29	14.21	4.79	1347.00
17:30	14.28	4.73	1370.00
17:31	14.27	4.73	1377.00
17:32	14.29	4.71	1378.00
17:33	14.23	4.74	1412.00
17:34	14.39	4.60	1443.00
17:35	14.37	4.62	1457.00
17:36	14.33	4.65	1486.00
17:37	14.23	4.73	1477.00
17:38	14.22	4.73	1474.00
17:39	14.12	4.81	1469.00
17:40	14.09	4.84	1469.00
17:41	14.04	4.87	1457.00
17:42	14.09	4.85	1471.00
17:43	14.03	4.89	1450.00
17:44	13.99	4.92	1471.00
17:45	14.06	4.86	1459.00
17:46	14.00	4.90	1449.00
17:47	13.85	5.02	1449.00
17:48	13.87	5.02	1413.00
17:49	13.71	5.15	1416.00
17:50	13.65	5.20	1428.00
17:51	13.52	5.30	1425.00
17:52	13.49	5.34	1441.00
17:53	13.48	5.33	1444.00
17:54	13.50	5.31	1453.00
17:55	13.48	5.35	1442.00
17:56	13.42	5.39	1461.00
17:57	13.39	5.40	1465.00
17:58	13.30	5.48	1449.00
17:59	13.27	5.52	1478.00
18:00	13.24	5.54	1475.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 2A
JULY 20, 1999

Starting
07-20-99

Time	O2 % dv	CO2 %dv	CO ppmdv
18:01	13.32	5.50	1465.00
18:02	13.40	5.42	1478.00
18:03	13.42	5.41	1467.00
18:04	13.46	5.39	1460.00
18:05	13.36	5.45	1463.00
18:06	13.43	5.39	1470.00
18:07	13.47	5.37	1482.00
18:08	13.44	5.41	1513.00
18:09	13.52	5.35	1543.00
18:10	13.55	5.33	1551.00
18:11	13.58	5.28	1564.00
18:12	13.54	5.33	1607.00
18:13	13.55	5.32	1599.00
18:14	13.52	5.34	1563.00
18:15	13.53	5.35	1570.00
195 MinAvg	13.77	5.18	1416.02

Data Corrected for Calibrations
195 MinAvg   13.57   5.13   1392.23

METROPOLITAN SEWER DISTRICT
          SEWAGE SLUDGE INCINERATOR - RUN 2A
               JULY 20, 1999

     Calibrations:


```
[CO2      ]        Span Value =   20
LOW Calibration Gas =    0.00    HIGH Calibration Gas =   11.01

INITIAL CALIBRATION TIME --> 1424
  LOW Cal. Response =    0.12    HIGH Cal. Response =   10.99
FINAL CALIBRATION TIME ----> 1823
  LOW Cal. Response =    0.15    HIGH Cal. Response =   10.93
_____

  LOW System Drift =    0.13 %   HIGH System Drift =   -0.34 %
```


```
[CO      ]        Span Value =  6000
LOW Calibration Gas =-   0.00    HIGH Calibration Gas = 1809.00

INITIAL CALIBRATION TIME --> 1424
  LOW Cal. Response =    4.13    HIGH Cal. Response = 1847.30
FINAL CALIBRATION TIME ----> 1823
  LOW Cal. Response =    0.00    HIGH Cal. Response = 1831.30
_____

  LOW System Drift =   -0.07 %   HIGH System Drift =   -0.27 %
```


```
[O2      ]        Span Value =   25
LOW Calibration Gas =    0.00    HIGH Calibration Gas-=   11.5(

INITIAL CALIBRATION TIME --> 1424
  LOW Cal. Response =    0.17    HIGH Cal. Response =   11.80
FINAL CALIBRATION TIME ----> 1823
  LOW Cal. Response =    0.11    HIGH Cal. Response =   11.59
_____

  LOW System Drift =   -0.21 %   HIGH System Drift =   -0.83 %
```

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 2b
JULY 20, 1999

Starting
07-20-99

Time	O2 % dv	CO2 %dv	CO ppmdv
18:31	13.37	5.74	1422.00
18:32	13.45	5.69	1439.00
18:33	13.44	5.70	1430.00
18:34	13.38	5.76	1419.00
18:35	13.47	5.67	1421.00
18:36	13.58	5.58	1430.00
18:37	13.56	5.59	1415.00
18:38	13.57	5.59	1406.00
18:39	13.64	5.53	1378.00
18:40	13.68	5.50	1387.00
18:41	13.69	5.49	1389.00
18:42	13.70	5.50	1375.00
18:43	13.76	5.45	1373.00
18:44	13.81	5.40	1389.00
18:45	13.92	5.32	1397.00
18:46	13.88	5.34	1412.00
18:47	13.84	5.36	1415.00
18:48	13.90	5.30	1426.00
18:49	13.91	5.31	1440.00
18:50	13.91	5.31	1441.00
18:51	13.93	5.28	1434.00
18:52	13.94	5.26	1435.00
18:53	13.93	5.27	1433.00
18:54	13.94	5.26	1426.00
18:55	14.01	5.22	1410.00
18:56	14.10	5.14	1375.00
18:57	13.99	5.23	1356.00
18:58	14.02	5.23	1353.00
18:59	14.12	5.14	1341.00
19:00	14.11	5.14	1354.00
19:01	14.10	5.15	1374.00
19:02	14.08	5.16	1374.00
19:03	14.11	5.14	1382.00
19:04	14.10	5.15	1379.00
19:05	14.14	5.12	1387.00
19:06	14.14	5.13	1389.00
19:07	14.13	5.12	1418.00
19:08	14.24	5.03	1449.00
19:09	14.26	5.03	1453.00
19:10	14.26	5.00	1453.00
19:11	14.29	4.99	1446.00
19:12	14.33	4.97	1428.00
19:13	14.35	4.95	1426.00
19:14	14.34	4.95	1394.00
19:15	14.32	4.97	1386.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 2b
JULY 20, 1999

Starting
07-20-99

Time	O2 % dv	CO2 %dv	CO ppmdv
19:16	14.36	4.93	1398.00
19:17	14.39	4.92	1402.00
19:18	14.46	4.85	1390.00
19:19	14.45	4.86	1404.00
19:20	14.40	4.89	1405.00
19:21	14.39	4.91	1395.00
19:22	14.34	4.96	1402.00
19:23	14.29	5.00	1397.00
19:24	14.25	5.03	1397.00
19:25	14.24	5.03	1423.00
19:26	14.28	5.01	1435.00
19:27	14.31	4.98	1445.00
19:28	14.29	5.00	1438.00
19:29	14.31	4.97	1424.00
19:30	14.15	5.11	1416.00
19:31	14.08	5.16	1442.00
19:32	14.03	5.22	1442.00
19:33	13.98	5.27	1414.00
19:34	13.91	5.33	1390.00
19:35	13.94	5.31	1383.00
19:36	13.92	5.33	1381.00
19:37	13.80	5.43	1370.00
19:38	13.67	5.55	1365.00
19:39	13.60	5.63	1360.00
19:40	13.60	5.64	1350.00
19:41	13.59	5.65	1376.00
19:42	13.65	5.60	1395.00
19:43	13.62	5.61	1431.00
19:44	13.46	5.74	1450.00
19:45	13.50	5.73	1482.00
19:46	13.48	5.75	1483.00
19:47	13.54	5.71	1456.00
19:48	13.62	5.61	1450.00
19:49	13.60	5.63	1479.00
19:50	13.59	5.65	1502.00
19:51	13.52	5.72	1510.00
19:52	13.48	5.74	1505.00
19:53	13.55	5.68	1502.00
19:54	13.58	5.67	1475.00
19:55	13.60	5.67	1453.00
19:56	13.56	5.70	1429.00
19:57	13.62	5.66	1423.00
19:58	13.64	5.64	1394.00
19:59	13.63	5.65	1383.00
20:00	13.59	5.68	1384.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 2b
JULY 20, 1999

Starting
07-20-99

Time	O2 % dv	CO2 %dv	CO ppmdv
20:01	13.61	5.69	1374.00
20:02	13.56	5.70	1381.00
20:03	13.59	5.69	1373.00
20:04	13.63	5.64	1348.00
20:05	13.62	5.66	1358.00
20:06	13.69	5.61	1356.00
20:07	13.69	5.61	1343.00
20:08	13.87	5.46	1359.00
20:09	13.94	5.42	1370.00
20:10	13.93	5.43	1382.00
20:11	13.89	5.48	1396.00
20:12	13.99	5.42	1432.00
20:13	14.15	5.28	1418.00
20:14	14.20	5.25	1397.00
20:15	14.16	5.27	1421.00
20:16	14.24	5.22	1409.00
20:17	14.34	5.14	1383.00
20:18	14.40	5.09	1370.00
20:19	14.39	5.08	1358.00
20:20	14.39	5.08	1374.00
20:21	14.45	5.01	1374.00
20:22	14.37	5.08	1343.00
20:23	14.39	5.06	1312.00
20:24	14.37	5.06	1307.00
20:25	14.45	4.98	1303.00
20:26	14.49	4.94	1302.00
20:27	14.46	4.96	1295.00
20:28	14.36	5.02	1300.00
20:29	14.29	5.10	1321.00
20:30	14.38	5.01	1335.00
20:31	14.36	5.02	1308.00
20:32	14.33	5.03	1305.00
20:33	14.36	5.00	1318.00
20:34	14.43	4.95	1340.00
20:35	14.36	5.00	1343.00
20:36	14.35	5.01	1356.00
20:37	14.31	5.03	1340.00
20:38	14.29	5.04	1333.00
20:39	14.32	5.01	1332.00
20:40	14.31	5.02	1341.00
20:41	14.34	4.99	1360.00
20:42	14.26	5.05	1374.00
20:43	14.33	4.99	1374.00
20:44	14.27	5.06	1375.00
20:45	14.31	5.01	1373.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 2b
JULY 20, 1999

Starting
07-20-99

Time	O2 % dv	CO2 %dv	CO ppmdv
20:46	14.24	5.04	1381.00
20:47	14.26	5.04	1403.00
20:48	14.30	5.01	1425.00
20:49	14.33	4.97	1440.00
20:50	14.33	4.97	1450.00
20:51	14.32	5.00	1462.00
20:52	14.30	5.00	1449.00
20:53	14.29	5.02	1446.00
20:54	14.26	5.03	1456.00
20:55	14.13	5.14	1443.00
20:56	14.18	5.10	1428.00
20:57	14.11	5.15	1421.00
20:58	14.08	5.19	1419.00
20:59	14.01	5.25	1396.00
21:00	14.04	5.22	1401.00
21:01	13.91	5.33	1373.00
21:02	13.89	5.35	1375.00
21:03	13.88	5.35	1382.00
21:04	13.89	5.34	1371.00
21:05	13.84	5.39	1372.00
21:06	13.74	5.48	1356.00
21:07	13.75	5.49	1385.00
21:08	13.72	5.51	1389.00
21:09	13.69	5.53	1368.00
21:10	13.71	5.52	1353.00
21:11	13.78	5.47	1363.00
21:12	13.83	5.43	1348.00
21:13	13.93	5.35	1340.00
21:14	13.86	5.39	1332.00
21:15	13.91	5.36	1298.00
21:16	13.96	5.31	1268.00
21:17	14.01	5.29	1276.00
21:18	14.09	5.22	1264.00
21:19	14.11	5.22	1249.00
21:20	14.19	5.16	1253.00
21:21	14.26	5.12	1268.00
21:22	14.31	5.08	1263.00
21:23	14.34	5.06	1265.00
21:24	14.44	5.00	1258.00
21:25	14.50	4.96	1258.00
21:26	14.57	4.91	1270.00
21:27	14.59	4.89	1272.00
21:28	14.60	4.89	1256.00
21:29	14.62	4.87	1266.00
21:30	14.71	4.80	1266.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 2b
JULY 20, 1999

Starting
07-20-99

Time	O2 % dv	CO2 %dv	CO ppmdv
180 MinAvg	14.03	5.26	1383.51

Data Corrected for Calibrations
180 MinAvg	13.92	5.19	1366.72

METROPOLITAN SEWER DISTRICT
            SEWAGE SLUDGE INCINERATOR - RUN 2b
                   JULY 20, 1999

    Calibrations:

    [CO2   ]   Span Value = -20
    LOW Calibration Gas =   0.00   HIGH Calibration Gas =   11.01

    INITIAL CALIBRATION TIME --> 1823
      LOW Cal. Response =   0.15   HIGH Cal. Response =   10.93
    FINAL CALIBRATION TIME ----> 2138
      LOW Cal. Response =   0.14   HIGH Cal. Response =   11.05
    ───
      LOW System Drift =   -0.07 %   HIGH System Drift =   0.63 %

    [CO   ]   Span Value = 6000
    LOW Calibration Gas =   0.00   HIGH Calibration Gas = 1809.00

    INITIAL CALIBRATION TIME --> 1823
      LOW Cal. Response =   0.00   HIGH Cal. Response = 1831.30
    FINAL CALIBRATION TIME ----> 2138
      LOW Cal. Response =   0.77   HIGH Cal. Response = 1830.90
    ───
      LOW System Drift =   0.01 %   HIGH System Drift =   -0.01 %

    [O2   ]   Span Value = 25
    LOW Calibration Gas =   0.00   HIGH Calibration Gas =   11.50

    INITIAL CALIBRATION TIME --> 1823
      LOW Cal. Response =   0.11   HIGH Cal. Response =   11.59
    FINAL CALIBRATION TIME ----> 2138
      LOW Cal. Response =   0.07   HIGH Cal. Response =   11.62
    ───
      LOW System Drift =   -0.19 %   HIGH System Drift =   0.13 %

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 3A
JULY 21, 1999

Starting
07-21-99

Time	O2 % dv	CO2 %dv	CO ppmdv
10:16	14.86	4.49	1598.00
10:17	14.93	4.43	1628.00
10:18	14.81	4.53	1617.00
10:19	14.72	4.60	1594.00
10:20	14.68	4.64	1570.00
10:21	14.65	4.67	1560.00
10:22	14.63	4.68	1568.00
10:23	14.65	4.64	1592.00
10:24	14.65	4.64	1587.00
10:25	14.65	4.63	1589.00
10:26	14.66	4.63	1572.00
10:27	14.78	4.53	1582.00
10:28	14.94	4.39	1635.00
10:29	15.05	4.30	1691.00
10:30	15.14	4.22	1732.00
10:31	15.17	4.20	1766.00
10:32	15.03	4.28	1746.00
10:33	15.02	4.31	1721.00
10:34	14.96	4.37	1706.00
10:35	15.00	4.34	1692.00
10:36	14.94	4.37	1685.00
10:37	14.98	4.34	1693.00
10:38	15.09	4.26	1706.00
10:39	15.13	4.24	1684.00
10:40	15.13	4.22	1678.00
10:41	15.04	4.27	1669.00
10:42	14.98	4.33	1636.00
10:43	14.98	4.33	1627.00
10:44	14.79	4.46	1633.00
10:45	14.72	4.46	1637.00
10:46	14.16	4.83	1472.00
10:47	13.76	5.07	1281.00
10:48	13.41	5.28	1181.00
10:49	13.22	5.38	1070.00
10:50	13.21	5.38	1061.00
10:51	13.25	5.30	1060.00
10:52	13.17	5.34	1062.00
10:53	13.09	5.37	1079.00
10:54	12.88	5.51	1061.00
10:55	12.65	5.68	1033.00
10:56	12.39	5.89	1013.00
10:57	12.12	6.11	996.00
10:58	11.92	6.27	989.00
10:59	11.75	6.41	995.00
11:00	11.58	6.52	979.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR – RUN 3A
JULY 21, 1999

Starting
07-21-99

Time	O2 % dv	CO2 %dv	CO ppmdv
11:01	11.40	6.69	987.00
11:02	11.50	6.68	1016.00
11:03	11.90	6.49	1041.00
11:04	12.92	5.91	1114.00
11:05	13.28	5.64	1232.00
11:06	13.53	5.43	1251.00
11:07	13.72	5.28	1279.00
11:08	13.91	5.13	1292.00
11:09	14.02	5.04	1320.00
11:10	13.70	5.19	1320.00
11:11	13.61	5.24	1190.00
11:12	13.62	5.25	1160.00
11:13	13.64	5.23	1148.00
11:14	13.71	5.17	1160.00
11:15	13.81	5.09	1185.00
11:16	13.83	5.08	1212.00
11:17	13.75	5.14	1213.00
11:18	13.72	5.17	1227.00
11:19	13.77	5.11	1220.00
11:20	13.78	5.11	1233.00
11:21	13.68	5.21	1225.00
11:22	13.82	5.11	1215.00
11:23	13.98	4.97	1253.00
11:24	14.16	4.82	1336.00
11:25	14.18	4.82	1357.00
11:26	14.12	4.85	1342.00
11:27	14.12	4.83	1336.00
11:28	14.01	4.91	1341.00
11:29	13.99	4.92	1346.00
11:30	14.12	4.82	1349.00
11:31	14.21	4.75	1376.00
11:32	14.20	4.75	1405.00
11:33	14.32	4.66	1427.00
11:34	14.35	4.62	1439.00
11:35	14.31	4.65	1442.00
11:36	14.27	4.67	1462.00
11:37	14.28	4.65	1456.00
11:38	14.30	4.64	1478.00
11:39	14.37	4.56	1508.00
11:40	14.34	4.59	1505.00
11:41	14.37	4.57	1508.00
11:42	14.30	4.64	1504.00
11:43	14.24	4.67	1516.00
11:44	14.16	4.73	1519.00
11:45	14.04	4.84	1497.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 3A
JULY 21, 1999

Starting
07-21-99

Time	O2 % dv	CO2 %dv	CO ppmdv
11:46	14.02	4.85	1502.00
11:47	13.95	4.90	1494.00
11:48	13.99	4.86	1502.00
11:49	13.98	4.88	1508.00
11:50	13.99	4.87	1521.00
11:51	14.01	4.83	1531.00
11:52	13.93	4.90	1502.00
11:53	13.93	4.87	1511.00
11:54	13.64	5.01	1549.00
11:55	13.09	5.38	1366.00
11:56	12.78	5.61	1296.00
11:57	12.44	5.86	1245.00
11:58	12.13	6.11	1248.00
11:59	11.78	6.36	1246.00
12:00	11.40	6.66	1257.00
12:01	10.95	7.00	1306.00
12:02	10.46	7.41	1362.00
12:03	9.92	7.85	1539.00
12:04	9.60	8.18	1749.00
12:05	9.86	8.14	2137.00
12:06	10.24	7.98	1886.00
12:07	11.21	7.30	1727.00
12:08	12.03	6.64	1506.00
12:09	12.78	6.06	1321.00
12:10	13.37	5.57	1262.00
12:11	13.70	5.28	1222.00
12:12	13.90	5.10	1218.00
12:13	13.86	5.13	1225.00
12:14	13.34	5.44	1198.00
12:15	12.02	6.38	1159.00
12:16	11.75	6.63	1162.00
12:17	11.83	6.63	1170.00
12:18	12.12	6.44	1173.00
12:19	12.43	6.20	1151.00
12:20	12.65	6.05	1154.00
12:21	12.89	5.86	1153.00
12:22	13.04	5.75	1136.00
12:23	13.19	5.63	1111.00
12:24	13.21	5.61	1124.00
12:25	13.22	5.59	1130.00
12:26	13.18	5.60	1103.00
12:27	13.16	5.62	1094.00
12:28	13.20	5.56	1102.00
12:29	13.22	5.55	1134.00
12:30	13.17	5.59	1117.00

Starting
07-21-99

Time	O2 % dv	CO2 %dv	CO ppmdv
12:31	13.17	5.57	1118.00
12:32	13.26	5.50	1141.00
12:33	13.27	5.49	1147.00
12:34	13.34	5.43	1136.00
12:35	13.29	5.46	1144.00
12:36	13.39	5.35	1144.00
12:37	13.33	5.40	1108.00
12:38	13.20	5.48	1094.00
12:39	13.04	5.58	1093.00
12:40	13.00	5.59	1079.00
12:41	12.84	5.71	1053.00
12:42	12.76	5.74	1022.00
12:43	12.70	5.79	1012.00
12:44	12.83	5.72	1022.00
12:45	12.89	5.72	1040.00
12:46	13.05	5.65	1042.00
12:47	13.03	5.65	1021.00
12:48	13.04	5.65	1025.00
12:49	13.00	5.65	1024.00
12:50	12.93	5.70	1026.00
12:51	13.05	5.60	1043.00
12:52	13.09	5.60	1026.00
12:53	13.03	5.63	1040.00
12:54	13.01	5.63	1051.00
12:55	13.05	5.60	1044.00
12:56	13.08	5.60	1030.00
12:57	13.18	5.53	1016.00
12:58	13.19	5.52	1022.00
12:59	13.22	5.49	1019.00
13:00	13.18	5.51	1013.00
13:01	13.24	5.46	1011.00
13:02	13.30	5.40	980.00
13:03	13.29	5.42	970.00
13:04	13.31	5.37	957.00
13:05	13.28	5.41	960.00
13:06	13.29	5.40	980.00
13:07	13.27	5.39	978.00
13:08	13.27	5.39	974.00
13:09	13.31	5.38	966.00
13:10	13.27	5.41	947.00
13:11	13.30	5.37	965.00
13:12	13.31	5.37	965.00
13:13	13.35	5.32	947.00
13:14	13.29	5.38	944.00
13:15	13.30	5.37	927.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 3A
JULY 21, 1999

Starting
07-21-99

Time	O2 % .dv	CO2 %dv	CO ppmdv
180 MinAvg	13.45	5.34	1283.57

Data Corrected for Calibrations
180 MinAvg	13.32	5.35	1244.74

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR – RUN 3B
JULY 21, 1999

Starting
07-21-99

Time	O2 % dv	CO2 %dv	CO ppmdv
13:36	13.13	4.96	918.00
13:37	13.11	4.94	946.00
13:38	13.09	4.97	946.00
13:39	13.10	4.95	955.00
13:40	13.12	4.95	949.00
13:41	13.12	4.93	946.00
13:42	13.10	4.95	946.00
13:43	13.28	4.93	947.00
13:44	13.58	5.02	969.00
13:45	13.54	5.08	953.00
13:46	13.54	5.06	966.00
13:47	13.54	5.07	991.00
13:48	13.45	5.14	1022.00
13:49	13.45	5.14	1039.00
13:50	13.47	5.12	1024.00
13:51	13.44	5.16	1035.00
13:52	13.37	5.18	1040.00
13:53	12.96	5.45	1055.00
13:54	12.76	5.62	1067.00
13:55	12.78	5.61	1084.00
13:56	12.71	5.66	1078.00
13:57	12.70	5.69	1064.00
13:58	12.60	5.75	1067.00
13:59	12.49	5.84	1072.00
14:00	12.42	5.91	1097.00
14:01	12.42	5.94	1144.00
14:02	12.44	5.94	1153.00
14:03	12.45	5.95	1139.00
14:04	12.45	5.94	1137.00
14:05	12.43	5.96	1177.00
14:06	12.29	6.08	1177.00
14:07	12.28	6.10	1175.00
14:08	12.12	6.22	1176.00
14:09	12.05	6.29	1180.00
14:10	11.85	6.46	1194.00
14:11	11.69	6.57	1221.00
14:12	11.58	6.65	1210.00
14:13	11.50	6.73	1211.00
14:14	11.42	6.79	1203.00
14:15	11.34	6.90	1222.00
14:16	11.32	6.90	1210.00
14:17	11.33	6.91	1190.00
14:18	11.32	6.89	1187.00
14:19	11.32	6.91	1187.00
14:20	11.35	6.89	1183.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR – RUN 3B
JULY 21, 1999

Starting
07-21-99

Time	O2 % dv	CO2 %dv	CO ppmdv
14:21	11.36	6.91	1195.00
14:22	11.45	6.81	1188.00
14:23	11.46	6.81	1183.00
14:24	11.55	6.77	1173.00
14:25	11.68	6.67	1161.00
14:26	11.76	6.62	1157.00
14:27	11.77	6.60	1163.00
14:28	12.00	6.46	1159.00
14:29	13.09	5.73	1190.00
14:30	13.33	5.55	1265.00
14:31	13.42	5.47	1263.00
14:32	13.46	5.42	1276.00
14:33	13.50	5.37	1298.00
14:34	13.55	5.32	1293.00
14:35	13.48	5.36	1290.00
14:36	13.53	5.32	1296.00
14:37	13.55	5.30	1267.00
14:38	13.53	5.30	1253.00
14:39	13.46	5.36	1237.00
14:40	13.51	5.32	1233.00
14:41	13.49	5.32	1241.00
14:42	13.49	5.32	1262.00
14:43	13.51	5.30	1258.00
14:44	13.55	5.26	1243.00
14:45	13.58	5.24	1250.00
14:46	13.53	5.26	1251.00
14:47	13.57	5.23	1249.00
14:48	13.61	5.18	1246.00
14:49	13.58	5.21	1259.00
14:50	13.61	5.19	1241.00
14:51	13.52	5.26	1244.00
14:52	13.48	5.28	1249.00
14:53	13.49	5.27	1222.00
14:54	13.55	5.22	1230.00
14:55	13.52	5.25	1216.00
14:56	13.51	5.26	1194.00
14:57	13.49	5.29	1180.00
14:58	13.50	5.29	1164.00
14:59	13.48	5.29	1144.00
15:00	13.54	5.25	1133.00
15:01	13.56	5.22	1132.00
15:02	13.56	5.22	1145.00
15:03	13.58	5.19	1136.00
15:04	13.56	5.22	1119.00
15:05	13.59	5.20	1100.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR – RUN 3B
JULY 21, 1999

Starting
07-21-99

Time	O2 %.dv	CO2 %dv	CO ppmdv
15:06	13.66	5.13	1106.00
15:07	13.57	5.17	1115.00
15:08	12.55	5.87	1097.00
15:09	12.48	5.95	1061.00
15:10	12.49	5.95	1043.00
15:11	12.44	5.99	1026.00
15:12	12.54	5.92	1041.00
15:13	12.51	5.94	1038.00
15:14	12.56	5.91	1041.00
15:15	12.60	5.88	1053.00
15:16	12.63	5.86	1052.00
15:17	12.69	5.83	1065.00
15:18	12.75	5.77	1067.00
15:19	12.85	5.66	1076.00
15:20	12.82	5.70	1069.00
15:21	12.89	5.64	1068.00
15:22	12.95	5.59	1074.00
15:23	13.06	5.49	1067.00
15:24	13.06	5.50	1059.00
15:25	13.09	5.47	1075.00
15:26	13.16	5.41	1071.00
15:27	13.18	5.38	1067.00
15:28	13.13	5.41	1067.00
15:29	13.14	5.40	1064.00
15:30	13.21	5.36	1049.00
15:31	13.17	5.38	1036.00
15:32	13.16	5.38	1051.00
15:33	13.24	5.30	1033.00
15:34	13.24	5.29	1039.00
15:35	13.17	5.34	1032.00
15:36	13.14	5.36	1029.00
15:37	13.14	5.35	1030.00
15:38	13.04	5.43	1011.00
15:39	13.06	5.41	1012.00
15:40	13.14	5.36	1007.00
15:41	13.19	5.30	986.00
15:42	13.08	5.38	989.00
15:43	13.06	5.39	987.00
15:44	13.07	5.37	1007.00
15:45	13.13	5.32	1022.00
15:46	13.07	5.39	1019.00
15:47	13.09	5.35	1024.00
15:48	13.10	5.33	1035.00
15:49	13.16	5.29	1044.00
15:50	13.15	5.30	1043.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR – RUN 3B
JULY 21, 1999

Starting
07-21-99

Time	O2 % dv	CO2 %dv	CO ppmdv
15:51	13.11	5.31	1056.00
15:52	13.09	5.32	1078.00
15:53	13.05	5.34	1075.00
15:54	13.06	5.33	1067.00
15:55	13.09	5.32	1067.00
15:56	13.13	5.29	1067.00
15:57	13.04	5.36	1062.00
15:58	13.05	5.33	1072.00
15:59	13.01	5.35	1098.00
16:00	12.96	5.39	1105.00
16:01	12.90	5.44	1111.00
16:02	12.90	5.45	1120.00
16:03	12.78	5.53	1117.00
16:04	12.71	5.59	1117.00
16:05	12.62	5.65	1107.00
16:06	12.62	5.66	1120.00
16:07	12.59	5.68	1119.00
16:08	12.48	5.77	1144.00
16:09	12.34	5.88	1139.00
16:10	12.27	5.94	1150.00
16:11	12.28	5.92	1153.00
16:12	12.13	6.05	1157.00
16:13	12.11	6.07	1139.00
16:14	12.03	6.12	1140.00
16:15	11.99	6.18	1135.00
16:16	11.93	6.22	1127.00
16:17	11.85	6.28	1136.00
16:18	11.85	6.28	1127.00
16:19	11.74	6.37	1124.00
16:20	11.71	6.40	1119.00
16:21	11.65	6.44	1099.00
16:22	11.57	6.51	1090.00
16:23	11.57	6.51	1089.00
16:24	11.70	6.43	1081.00
16:25	11.51	6.60	1067.00
16:26	11.57	6.55	1051.00
16:27	12.09	6.24	1053.00
16:28	12.87	5.67	1151.00
16:29	12.95	5.62	1186.00
16:30	12.99	5.59	1184.00
16:31	13.00	5.58	1178.00
16:32	12.99	5.57	1181.00
16:33	13.03	5.55	1167.00
16:34	13.07	5.51	1178.00
16:35	13.12	5.46	1190.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 3B
JULY 21, 1999

Starting
07-21-99

Time	O2 % dv	CO2 %dv	CO ppmdv
180 MinAvg	12.80	5.66	1115.78

Data Corrected for Calibrations
180 MinAvg   12.74   5.66   1095.76

TROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 3B
JULY 21, 1999

Calibrations:

[CO2   ]   Span Value =   20
LOW Calibration Gas =   0.00   HIGH Calibration Gas =   11.01

INITIAL CALIBRATION TIME --> 1326
  LOW Cal. Response =   0.15   HIGH Cal. Response =   10.88
FINAL CALIBRATION TIME ----> 1643
  LOW Cal. Response =   0.14   HIGH Cal. Response =   10.89
_____
  LOW System Drift =   -0.04 %   HIGH System Drift =   0.06 %

[CO   ]   Span Value =   6000
LOW Calibration Gas =   0.00   HIGH Calibration Gas = 1809.00

IITIAL CALIBRATION TIME --> 1326
  LOW Cal. Response =   ·2.06   HIGH Cal. Response = 1851.50
FINAL CALIBRATION TIME ----> 1643
  LOW Cal. Response =   0.26   HIGH Cal. Response = 1831.10
_____
  LOW System Drift =   -0.03 %   HIGH System Drift =   -0.34 %

[O2   ]   Span Value =   25
LOW Calibration Gas =   0.00   HIGH Calibration Gas =   11.50

INITIAL CALIBRATION TIME --> 1326
  LOW Cal. Response =   0.11   HIGH Cal. Response =   11.70
FINAL CALIBRATION TIME ----> 1643
  LOW Cal. Response =   0.12   HIGH Cal. Response =   11.44
_____
  LOW System Drift =   0.07 %   HIGH System Drift =   -1.03 %

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 4A
JULY 22, 1999

Starting
07-22-99

Time	O2 % dv	CO2 %dv	CO ppmdv
08:16	12.98	5.43	1372.00
08:17	12.93	5.48	1351.00
08:18	12.97	5.46	1351.00
08:19	12.91	5.51	1332.00
08:20	12.91	5.50	1313.00
08:21	12.88	5.51	1311.00
08:22	12.91	5.52	1316.00
08:23	12.95	5.47	1309.00
08:24	13.01	5.45	1289.00
08:25	12.97	5.47	1281.00
08:26	12.98	5.48	1263.00
08:27	12.98	5.49 --	1258.00
08:28	13.05	5.45	1257.00
08:29	13.04	5.43	1258.00
08:30	13.13	5.38	1253.00
08:31	13.12	5.38	1230.00
08:32	13.10	5.39	1216.00
08:33	13.13	5.36	1211.00
08:34	13.12	5.39	1184.00
08:35	13.02	5.47	1146.00
08:36	12.99	5.50	1115.00
08:37	13.00	5.47	1119.00
08:38	12.95	5.51	1117.00
08:39	12.91	5.55	1116.00
08:40	12.98	5.51	1097.00
08:41	13.33	5.51	1097.00
08:42	13.72	5.43	1100.00
08:43	13.79	5.38	1102.00
08:44	13.98	5.22	1096.00
08:45	14.07	5.16	1106.00
08:46	14.14	5.11	1096.00
08:47	14.27	5.02	1096.00
08:48	14.40	4.93	1082.00
08:49	14.47	4.86	1067.00
08:50	14.53	4.80	1062.00
08:51	14.49	4.81	1067.00
08:52	14.41	4.84	1055.00
08:53	14.38	4.87	1065.00
08:54	14.40	4.88	1084.00
08:55	14.33	4.90	1086.00
08:56	14.25	4.96	1084.00
08:57	14.18	4.99	1075.00
08:58	14.16	4.99	1078.00
08:59	14.10	5.02	1082.00
09:00	14.05	5.05	1058.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR – RUN 4A
JULY 22, 1999

Starting
07-22-99

Time	O2 %.dv	CO2 %dv	CO ppmdv
09:01	14.09	5.01	1043.00
09:02	14.10	5.02	1056.00
09:03	14.14	4.97	1066.00
09:04	14.16	4.94	1089.00
09:05	14.24	4.89	1097.00
09:06	14.27	4.85	1110.00
09:07	14.27	4.85	1096.00
09:08	14.35	4.78	1114.00
09:09	14.42	4.76	1125.00
09:10	14.46	4.72	1129.00
09:11	14.55	4.65	1133.00
09:12	14.60	4.62	1131.00
09:13	14.57	4.65	1138.00
09:14	14.60	4.61	1132.00
09:15	14.59	4.63	1143.00
09:16	14.60	4.63	1176.00
09:17	14.63	4.60	1182.00
09:18	14.64	4.59	1204.00
09:19	14.67	4.56	1224.00
09:20	14.65	4.58	1249.00
09:21	14.58	4.63	1226.00
09:22	14.55	4.67	1202.00
09:23	14.57	4.64	1184.00
09:24	14.57	4.64	1172.00
09:25	14.56	4.64	1172.00
09:26	14.51	4.69	1156.00
09:27	14.48	4.70	1145.00
09:28	14.39	4.78	1143.00
09:29	14.38	4.80	1136.00
09:30	14.35	4.80	1134.00
09:31	14.36	4.82	1136.00
09:32	14.32	4.85	1139.00
09:33	14.23	4.90	1130.00
09:34	14.28	4.87	1160.00
09:35	14.31	4.86	1181.00
09:36	14.36	4.80	1179.00
09:37	14.31	4.84	1182.00
09:38	14.36	4.81	1180.00
09:39	14.32	4.83	1213.00
09:40	14.34	4.81	1216.00
09:41	14.25	4.88	1202.00
09:42	14.19	4.92	1185.00
09:43	14.12	4.97	1192.00
09:44	14.07	5.00	1185.00
09:45	13.99	5.05	1183.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 4A
JULY 22, 1999

Starting
07-22-99

Time	O2 % dv	CO2 %dv	CO ppmdv
180 MinAvg	13.95	5.05	1152.38

Data Corrected for Calibrations
180 MinAvg	13.87	5.05	1136.17

SEWAGE SLUDGE INCINERATOR - RUN 4A
JULY 22, 1999

Calibrations:

```
[CO2    ]        Span Value =   20
LOW Calibration Gas =    0.00     HIGH Calibration Gas =    11.01

INITIAL CALIBRATION TIME --> 707
  LOW Cal. Response =    0.11     HIGH Cal. Response =    10.85
FINAL CALIBRATION TIME ----> 1123
  LOW Cal. Response =    0.13     HIGH Cal. Response =    10.91
─────────────────────────────────────────────────────────────────
  LOW System Drift =    0.11 %   HIGH System Drift =    0.29 %
```

```
[CO     ]        Span Value = 6000
LOW Calibration Gas =    0.00     HIGH Calibration Gas = 1809.00

INITIAL CALIBRATION TIME --> 707
  LOW Cal. Response =    5.42     HIGH Cal. Response = 1831.90
FINAL CALIBRATION TIME ----> 1123
  LOW Cal. Response =    5.42     HIGH Cal. Response = 1831.30
─────────────────────────────────────────────────────────────────
  LOW System Drift =   -0.00 %   HIGH System Drift =   -0.01 %
```

```
[O2     ]        Span Value =   25
LOW Calibration Gas =    0.00     HIGH Calibration Gas =    11.50

INITIAL CALIBRATION TIME --> .707
  LOW Cal. Response =    0.06     HIGH Cal. Response =    11.43
FINAL CALIBRATION TIME ----> 1123
  LOW Cal. Response =    0.11     HIGH Cal. Response =    11.73
─────────────────────────────────────────────────────────────────
  LOW System Drift =    0.20 %   HIGH System Drift =    1.22 %
```

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 4B
JULY 22, 1999

Starting
07-22-99

Time	O2 % dv	CO2 %dv	CO ppmdv
11:36	12.36	5.03	1146.00
11:37	12.88	5.08	1157.00
11:38	12.78	5.14	1146.00
11:39	12.83	5.15	1146.00
11:40	12.86	5.10	1154.00
11:41	12.85	5.12	1154.00
11:42	12.77	5.18	1154.00
11:43	12.74	5.24	1131.00
11:44	12.83	5.16	1131.00
11:45	12.84	5.16	1142.00
11:46	12.90	5.10	1166.00
11:47	12.94	5.07	1192.00
11:48	12.92	5.10	1200.00
11:49	12.93	5.08	1208.00
11:50	12.92	5.09	1220.00
11:51	12.94	5.06	1224.00
11:52	12.90	5.10	1235.00
11:53	12.95	5.03	1237.00
11:54	12.91	5.06	1234.00
11:55	12.90	5.06	1227.00
11:56	12.82	5.12	1212.00
11:57	12.82	5.12	1187.00
11:58	12.81	5.13	1192.00
11:59	12.83	5.11	1212.00
12:00	12.80	5.13	1238.00
12:01	12.76	5.17	1248.00
12:02	12.78	5.14	1254.00
12:03	12.80	5.14	1247.00
12:04	12.76	5.16	1257.00
12:05	12.76	5.15	1283.00
12:06	12.71	5.19	1294.00
12:07	12.79	5.15	1309.00
12:08	12.73	5.18	1297.00
12:09	12.67	5.22	1279.00
12:10	12.64	5.26	1269.00
12:11	12.65	5.28	1266.00
12:12	12.68	5.24	1283.00
12:13	12.67	5.24	1294.00
12:14	12.73	5.20	1294.00
12:15	12.62	5.31	1284.00
12:16	12.62	5.31	1264.00
12:17	12.58	5.34	1254.00
12:18	12.60	5.33	1248.00
12:19	12.50	5.41	1234.00
12:20	12.49	5.43	1234.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 4B
JULY 22, 1999

Starting
07-22-99

Time	O2 % dv	CO2 %dv	CO ppmdv
12:21	12.51	5.41	1220.00
12:22	12.50	5.42	1185.00
12:23	12.41	5.47	1182.00
12:24	12.37	5.51	1180.00
12:25	12.44	5.45	1187.00
12:26	12.46	5.47	1185.00
12:27	12.62	5.32	1170.00
12:28	12.52	5.39	1127.00
12:29	12.62	5.34	1124.00
12:30	12.60	5.35	1134.00
12:31	12.97	5.42	1130.00
12:32	13.00	5.41	1116.00
12:33	13.05	5.37	1106.00
12:34	13.01	5.41	1103.00
12:35	13.00	5.41	1093.00
12:36	13.13	5.31	1076.00
12:37	13.12	5.32	1067.00
12:38	13.18	5.28	1062.00
12:39	13.19	5.27	1057.00
12:40	13.25	5.22	1060.00
12:41	13.34	5.15	1066.00
12:42	13.39	5.09	1083.00
12:43	13.38	5.09	1110.00
12:44	13.40	5.07	1122.00
12:45	13.44	5.04	1145.00
12:46	13.39	5.07	1136.00
12:47	13.41	5.06	1137.00
12:48	13.42	5.04	1116.00
12:49	13.45	5.02	1128.00
12:50	13.46	5.00	1129.00
12:51	13.49	4.97	1132.00
12:52	13.50	4.96	1119.00
12:53	13.45	5.01	1111.00
12:54	13.51	4.95	1096.00
12:55	13.47	5.01	1093.00
12:56	13.49	5.00	1109.00
12:57	13.53	4.97	1093.00
12:58	13.61	4.90	1072.00
12:59	13.65	4.89	1062.00
13:00	13.64	4.90	1055.00
13:01	13.75	4.81	1053.00
13:02	13.72	4.84	1053.00
13:03	13.72	4.83	1064.00
13:04	13.76	4.82	1062.00
13:05	13.74	4.82	1067.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 4B
JULY 22, 1999

Starting
07-22-99

Time	O2 % dv	CO2 %dv	CO ppmdv
13:06	13.80	4.78	1076.00
13:07	13.76	4.81	1089.00
13:08	13.75	4.83	1109.00
13:09	13.69	4.86	1097.00
13:10	13.79	4.80	1113.00
13:11	13.72	4.85	1125.00
13:12	13.74	4.83	1142.00
13:13	13.69	4.88	1128.00
13:14	13.69	4.87	1117.00
13:15	13.69	4.89	1114.00
13:16	13.66	4.89	1116.00
13:17	13.70	4.89	1132.00
13:18	13.76	4.82	1126.00
13:19	13.81	4.79	1122.00
13:20	13.80	4.80	1117.00
13:21	13.79	4.82	1113.00
13:22	13.79	4.83	1111.00
13:23	13.72	4.87	1106.00
13:24	13.75	4.86	1098.00
13:25	13.75	4.87	1122.00
13:26	13.73	4.87	1120.00
13:27	13.69	4.92	1100.00
13:28	13.76	4.87	1114.00
13:29	13.71	4.89	1130.00
13:30	13.74	4.88	1123.00
13:31	13.67	4.93	1123.00
13:32	13.62	4.98	1114.00
13:33	13.61	4.97	1129.00
13:34	13.51	5.07	1114.00
13:35	13.46	5.10	1113.00
13:36	13.50	5.08	1131.00
13:37	13.54	5.05	1133.00
13:38	13.49	5.09	1143.00
13:39	13.59	5.02	1127.00
13:40	13.58	5.02	1138.00
13:41	13.47	5.10	1120.00
13:42	13.49	5.08	1132.00
13:43	13.54	5.06	1144.00
13:44	13.49	5.08	1133.00
13:45	13.48	5.09	1133.00
13:46	13.49	5.08	1143.00
13:47	13.46	5.09	1154.00
13:48	13.41	5.13	1151.00
13:49	13.35	5.17	1133.00
13:50	13.35	5.18	1133.00

METROPOLITAN SEWER DISTRICT
SEWAGE SLUDGE INCINERATOR - RUN 4B
JULY 22, 1999

Starting
07-22-99

Time	O2 % dv	CO2 %dv	CO ppmdv
13:51	13.26	5.26	1120.00
13:52	13.29	5.22	1142.00
13:53	13.35	5.18	1134.00
13:54	13.39	5.15	1115.00
13:55	13.37	5.15	1124.00
13:56	13.39	5.14	1123.00
13:57	13.35	5.15	1133.00
13:58	13.34	5.18	1136.00
13:59	13.34	5.18	1134.00
14:00	13.34	5.19	1133.00
14:01	13.36	5.16	1124.00
14:02	13.33	5.19	1118.00
14:03	13.33	5.19	1108.00
14:04	13.26	5.26	1071.00
14:05	13.29	5.23	1070.00
14:06	13.30	5.24	1087.00
14:07	13.38	5.18	1089.00
14:08	13.33	5.22	1086.00
14:09	13.27	5.27	1076.00
14:10	13.27	5.28	1080.00
14:11	13.24	5.31	1084.00
14:12	13.26	5.28	1082.00
14:13	13.23	5.33	1079.00
14:14	13.30	5.24	1086.00
14:15	13.06	5.44	1081.00
14:16	13.13	5.37	1067.00
14:17	13.03	5.46	1071.00
14:18	13.04	5.46	1082.00
14:19	13.05	5.43	1056.00
14:20	13.07	5.43	1070.00
14:21	13.04	5.46	1080.00
14:22	13.06	5.45	1061.00
14:23	13.12	5.40	1033.00
14:24	13.20	5.34	1027.00
14:25	13.27	5.28	1023.00
14:26	13.34	5.24	1044.00
14:27	13.41	5.19	1058.00
14:28	13.74	4.96	1093.00
14:29	14.02	4.76	1154.00
14:30	14.08	4.72	1163.00
14:31	14.23	4.61	1175.00
14:32	14.31	4.56	1184.00
14:33	14.38	4.51	1172.00
14:34	14.44	4.46	1164.00
14:35	14.54	4.37	1179.00

Calibrations:

```
[CO2      ]        Span Value =   20
LOW Calibration Gas =    0.00     HIGH Calibration Gas =   11.01

INITIAL CALIBRATION TIME --> 1123
  LOW Cal. Response =    0.13     HIGH Cal. Response =   10.91
FINAL CALIBRATION TIME ----> 1443
  LOW Cal. Response =    0.13     HIGH Cal. Response =   10.85
_____
  LOW System Drift =   -0.03 %   HIGH System Drift =   -0.32 %
```

```
[CO       ]        Span Value = 6000
LOW Calibration Gas =    0.00     HIGH Calibration Gas = 1809.00

INITIAL CALIBRATION TIME --> 1123
  LOW Cal. Response =    5.42     HIGH Cal. Response = 1831.30
FINAL CALIBRATION TIME ----> 1443
  LOW Cal. Response =    5.71     HIGH Cal. Response = 1853.80
_____
  LOW System Drift =    0.00 %   HIGH System Drift =    0.38 %
```

```
[O2       ]        Span Value =   25
LOW Calibration Gas =    0.00     HIGH Calibration Gas =   11.50

INITIAL CALIBRATION TIME --> 1123
  LOW Cal. Response =    0.11     HIGH Cal. Response =   11.73
FINAL CALIBRATION TIME ----> 1443
  LOW Cal. Response =    0.12     HIGH Cal. Response =   11.80
_____
  LOW System Drift =    0.03 %   HIGH System Drift =    0.27 %
```

L-3
CEM Response Time Determination

RESPONSE TIME DETERMINATION

FACILITY _Cincinnati MSD_

DATE _7/19/99_

ANALYZER TYPE _CO_

SPAN GAS CONCENTRATION _3005_

ANALYZER REPSONSE _2984_

UPSCALE RESPONSE TIME		DOWNSCALE RESPONSE TIME	
1	_155_ SECONDS	1	_144_ SECONDS
2	_154_ SECONDS	2	_146_ SECONDS
3	_145_ SECONDS	3	_142_ SECONDS
AVG.	_151.3_ SECONDS	AVG.	_144.0_ SECONDS

NTS:

(1) Upscale Response Time of 151.3 was the slowest response of all 3 analyzers. Rounded up to nearest minute. Used 3 minutes as response time for all continuous monitoring.

RESPONSE TIME DETERMINATION

FACILITY _Cincinnati MSD_

DATE _7/19/99_

ANALYZER TYPE_____ _CO₂_____

SPAN GAS CONCENTRATION_____ _18.0 % dc_

ANALYZER REPSONSE_____ _17.85 % dc_

UPSCALE RESPONSE TIME   DOWNSCALE RESPONSE TIME.

1   _124_ SECONDS   1   _126_ SECONDS

2   _114_ SECONDS   ↴   2   _126_ SECONDS

      _122_ SECONDS   3   _119_ SECONDS

AVG. _120.0_ SECONDS   AVG. _123.7_ SECONDS

COMMENTS:

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RESPONSE TIME DETERMINATION

FACILITY _Cincinnati MSD_

DATE _7/19/99_

ANALYZER TYPE_ O_2 _

SPAN GAS CONCENTRATION_ _21.0% dv_

ANALYZER REPSONSE_ _20.8% dv_

UPSCALE RESPONSE TIME

1 _135_ SECONDS

2 _117_ SECONDS

3 _126_ SECONDS

AVG. _126.0_ SECONDS

DOWNSCALE RESPONSE TIME

1 _116_ SECONDS

2 _118_ SECONDS

3 _109_ SECONDS

AVG. _114.3_ SECONDS

.......ITS:

L-4
CEM Calibration Records

EPA METHOD 20
INTERFERENCE RESPONSE TABLE

Date: 04/19/93
Analyzer Type: Carbon Dioxide # 5
Serial Number: 91-20-15
Span Value: 20 %

Test Gas Type	Concentration (ppmdv)	Analyzer Output	% of Span
CO	488	0.101	0.0051
O2	21.9	0.203	0.0102
SO2	231	-0.021	0.0011
NOx	232	-0.007	0.0004
Total			0.0166

% of Span = (Analyzer output response / Instrument span) x 100
The sum of the (% of Span) values should not exceed 2%.

METHOD 20
INTERFERENCE RESPONSE TABLE

DATE: __5/28/96__

ANALYZER TYPE: ___CO #1___

SERIAL NUMBER: __48-25815-222__

TEST GAS TYPE	CONCENTRATION (ppmdv)	ANALYZER OUTPUT	% OF SPAN
O_2 ALM 017478	21.9 %	0.080	.008
CO_2 ALM 028817	10.14 %	-0.035	-.0035
SO_2 ALM 045190	224	0.0	0.0
N_{ox} AAL 3884	226	-0.130	-0.013
TOTAL		-.085	-0.0085

% OF SPAN = (ANALYZER OUTPUT RESPONSE/INSTRUMENT SPAN) X 100

The sum of the (% of Span) values should not exceed 2%.

ANALYZER ID: CO #1 '18-25815-222		
UNITS: (PPMev)	SPAN: 1,000	
SOURCE ID: Interference Check		
LOCATION: ETS Shop T III		
TECHNICIAN: C.S.		
DATE(S): 5 / 28 / 96		

ANALYZER CALIBRATION

RANGE	GAS CYLINDER ID	GAS VALUE	ANALYZER RESPONSE	ERROR % SPAN	TIM
ZERO	N$_2$ AX 29117	0	0.001	0001	9:15
LOW	CO ALM 019286	298.2	300.0	.18	9:1
HIGH	CO ALM 044198	594	596.36	.236	9:19
OTHER	CO ALM 039316	845	841.8	.32	9:2

SYSTEM BIAS AND DRIFT			SYSTEM BIAS				SYSTEM DRIFT			
RUN ID	RANGE	ANALYZER RESPONSE	SYSTEM RESPONSE	ABSOLUTE ERROR	ERROR % SPAN	TIME	SYSTEM RESPONSE	ABSOLUTE ERROR	ERROR % SPAN	TIM
	ZERO									
	UPSCALE									
	ZERO									
	UPSCALE									
	ZERO									
	UPSCALE									
	ZERO									
	UPSCALE									
	ZERO									
	UPSCALE									
	ZERO									
	UPSCALE									

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METHOD 20
INTERFERENCE RESPONSE TABLE

DATE: 1/3/95

ANALYZER TYPE: O₂ #2

SERIAL NUMBER: 102469

TEST GAS TYPE	CONCENTRATION (ppmdv)	ANALYZER OUTPUT	% OF SPAN
SO₂ cyl.# 56AL 2156	224	0.02	0.1
NO_x cyl.# AUM00935I	223	0.01	0.0
CO cyl.# 56AL 1966	442	0.01	0.0
CO₂ cyl.# AUM028817	104 %	0.00	0.0
TOTAL			0.1

__% OF SPAN = (ANALYZER OUTPUT RESPONSE/INSTRUMENT SPAN) X 100

The sum of the (% of Span) values should not exceed 2%.

ANALYZER ID: $O_2 \cdot \#2$ 102469

UNITS: ?   SPAN: 25%

SOURCE ID:

LOCATION: ETS

TECHNICIAN: D. Vecellio

DATE(S): 01 / 03 / 95

ANALYZER CALIBRATION

RANGE	GAS CYLINDER ID	GAS VALUE	ANALYZER RESPONSE	ERROR % SPAN	TIME
ZERO	$N_2 \cdot AX$ 18304	0	0	0	13:30
LOW	Q-ALM045637	9.97	9.99	0.1	13:50
HIGH	Q-ALM044169	21.7	21.70	0	13:45
OTHER					

SYSTEM BIAS AND DRIFT			SYSTEM BIAS					SYSTEM DRIFT			
RUN ID	RANGE	ANALYZER RESPONSE	SYSTEM RESPONSE	ABSOLUTE ERROR	ERROR % SPAN	TIME		SYSTEM RESPONSE	ABSOLUTE ERROR	ERROR % SPAN	TIME
	ZERO										
	UPSCALE										
	ZERO										
	UPSCALE										
	ZERO										
	UPSCALE										
	ZERO										
	UPSCALE										
	ZERO										
	UPSCALE										
	ZERO										
	UPSCALE										

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L-5
CEM Calibration Gas Certification Records

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SPECTRA GASES

277 Coit St. • Irvington, NJ 07111 USA   Tel.: (973) 372-2060 • (800) 932-0624 • Fax: (973) 372-8551
Shipped From: 80 Industrial Drive • Alpha, N.J. 08865

CERTIFICATE OF ANALYSIS

EPA PROTOCOL MIXTURE
PROCEDURE # :   G1

CUSTOMER: ETS, INC
SGI ORDER # :   132640
ITEM# :   3
P.O.# :   6732

CYLINDER # :   CC90980
CYLINDER PRES: 2000 PSIG
CGA OUTLET: 350

CERTIFICATION DATE: 4/22/98
EXPIRATION DATE: 4/22/2001

CERTIFICATION HISTORY

COMPONENT	DATE OF ASSAY	MEAN CONCENTRATION	CERTIFIED CONCENTRATION	ANALYTICAL ACCURACY
Propane	4/22/98	86.6 ppm	86.6 ppm	+/- 1%

BALANCE   Nitrogen

REFERENCE STANDARDS

COMPONENT	SRM/NTRM#	CYLINDER#	CONCENTRATION
Propane	SRM-2643a	SX20148	99.1 ppm

INSTRUMENTATION

COMPONENT	MAKE/MODEL	SERIAL #	DETECTOR	CALIBRATION DATE(S)
Propane	H. Packard 6890	US00001434	GC - FID	3/25/98

THIS STANDARD WAS CERTIFIED ACCORDING TO THE EPA PROTOCOL PROCEDURES.
DO NOT USE THIS STANDARD IF THE CYLINDER PRESSURE IS LESS THAN 150 PSIG.

ANALYST: _____
         TED NEEME

DATE: 4/22/98

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SPECTRA GASES INC.

3434 Route 22 West • Branchburg, NJ 08876 USA Tel.: (908) 252-9300 • (800) 932-0624 • Fax: (908) 252-0811
Shipped From: 80 Industrial Drive • Alpha, NJ 08865

CERTIFICATE OF ANALYSIS

EPA PROTOCOL MIXTURE
PROCEDURE # :   G1

CUSTOMER:	ETS, INC
SGI ORDER # :	136421
ITEM# :	3
P.O.# :	6933

CYLINDER # :	CC94773
CYLINDER PRES:	2000 PSIG
CGA OUTLET:	350

CERTIFICATION DATE: 10/5/98
EXPIRATION DATE: 10/5/2001

CERTIFICATION HISTORY

COMPONENT	DATE OF ASSAY	MEAN CONCENTRATION	CERTIFIED CONCENTRATION	ANALYTICAL ACCURACY
Propane	10/5/98	124.6 ppm	124.6 ppm	+/- 1%

BALANCE   Nitrogen

PREVIOUS CERTIFICATION DATES: None

REFERENCE STANDARDS

COMPONENT	SRM/NTRM#	CYLINDER#	CONCENTRATION
Propane	GMIS-1	CC53375	1004 ppm

INSTRUMENTATION

COMPONENT	MAKE/MODEL	SERIAL #	DETECTOR	CALIBRATION DATE(S)
Propane	H. Packard 6890	US00001434	GC - FID	10/1/98

THIS STANDARD WAS CERTIFIED ACCORDING TO THE EPA PROTOCOL PROCEDURES.
DO NOT USE THIS STANDARD IF THE CYLINDER PRESSURE IS LESS THAN 160 PSIG.

ANALYST: _____   DATE:_____10/5/98_____
              TED NEEME

4064

SPECTRA GASES INC.

3434 Route 22 West • Branchburg, NJ 08876 USA Tel.: (908) 252-9300 • (800) 932-0624 • Fax: (908) 252-0811
Shipped From: 80 Industrial Drive • Alpha, NJ 08865

CERTIFICATE OF ANALYSIS

EPA PROTOCOL MIXTURE
PROCEDURE # : G1

CUSTOMER:	ETS, INC
SGI ORDER # :	142592
ITEM# :	8
P.O.# :	7212

CYLINDER # :	CC84936
CYLINDER PRES:	2000 PSIG
CGA OUTLET:	590

CERTIFICATION DATE: 5/14/99
EXPIRATION DATE: 5/14/2002

CERTIFICATION HISTORY

COMPONENT	DATE OF ASSAY	MEAN CONCENTRATION	CERTIFIED CONCENTRATION	ANALYTICAL ACCURACY
Carbon Dioxide	5/14/99	18.00 %	18.00 %	+/- 1%
Oxygen	5/14/99	21.0 %	21.0 %	+/- 1%

BALANCE   Nitrogen

PREVIOUS CERTIFICATION DATES: None

REFERENCE STANDARDS

COMPONENT	SRM/NTRM#	CYLINDER#	CONCENTRATION
Carbon Dioxide	NTRM-82745x	CC79944	20.00 %
Oxygen	NTRM-82659X	CC83900	22.80 %

INSTRUMENTATION

COMPONENT	MAKE/MODEL	SERIAL #	DETECTOR	CALIBRATION DATE(S)
Carbon Dioxide	Horiba VIA-510	571417045	NDIR	5/3/99
Oxygen	Horiba MPA-510	570694081	PM	5/3/99

THIS STANDARD WAS CERTIFIED ACCORDING TO THE EPA PROTOCOL PROCEDURES.
DO NOT USE THIS STANDARD IF THE CYLINDER PRESSURE IS LESS THAN 150 PSIG.

ANALYST: _____   DATE: _____ 5/14/99
              FRED PIKULA

L 56

SPECTRA GASES INC.

3434 Route 22 West • Branchburg, NJ 08876 USA Tel.: (908) 252-9300 • (800) 932-0624 • Fax: (908) 252-0811
Shipped From: 80 Industrial Drive • Alpha, NJ 08865

CERTIFICATE OF ANALYSIS

EPA PROTOCOL MIXTURE
PROCEDURE # : G1

CUSTOMER:	ETS, INC	**CYLINDER # :**	CC88474
SGI ORDER # :	139104	**CYLINDER PRES:**	2000 PSIG
ITEM# :	9	**CGA OUTLET:**	590
P.O.# :	7305		

CERTIFICATION DATE: 1/22/99
EXPIRATION DATE: 1/22/2002

CERTIFICATION HISTORY

COMPONENT	DATE OF ASSAY	MEAN CONCENTRATION	CERTIFIED CONCENTRATION	ANALYTICAL ACCURACY
Oxygen	1/22/99	11.50 %	11.50 %	+/- 1%
Carbon Dioxide	1/22/99	11.01 %	11.01 %	+/- 1%

BALANCE Nitrogen

PREVIOUS CERTIFICATION DATES: None

REFERENCE STANDARDS

COMPONENT	SRM/NTRM#	CYLINDER#	CONCENTRATION
Oxygen	NTRM-82659X	CC83900	22.80 %
Carbon Dioxide	NTRM-82745x	CC79944	20.00 %

INSTRUMENTATION

COMPONENT	MAKE/MODEL	SERIAL #	DETECTOR	CALIBRATION DATE(S)
Oxygen	Horiba MPA-510	570694081	PM	12/30/98
Carbon Dioxide	Horiba VIA-510	571417045	NDIR	1/20/99

THIS STANDARD WAS CERTIFIED ACCORDING TO THE EPA PROTOCOL PROCEDURES.
DO NOT USE THIS STANDARD IF THE CYLINDER PRESSURE IS LESS THAN 150 PSIG.

ANALYST: _____   DATE: _____1/22/99_____
FRED PIKULA

SPECTRA GASES INC.

3434 Route 22 West • Branchburg, NJ 08876 USA Tel.: (908) 252-9300 • (800) 932-0624 • Fax: (908) 252-0811
Shipped From: 80 Industrial Drive • Alpha, NJ 08865

CERTIFICATE OF ANALYSIS

EPA PROTOCOL MIXTURE
PROCEDURE # : G1

CUSTOMER:	ETS, INC
SGI ORDER # :	135096
ITEM# :	1
P.O.# :	6873

CYLINDER # :	CC79868
CYLINDER PRES:	2000 PSIG
CGA OUTLET:	350

CERTIFICATION DATE: 8/18/98
EXPIRATION DATE: 8/18/2001

CERTIFICATION HISTORY

COMPONENT	DATE OF ASSAY	MEAN CONCENTRATION	CERTIFIED CONCENTRATION	ANALYTICAL ACCURACY
Carbon Monoxide	8/11/98	914.0 ppm	915 ppm	+/- 1%
	8/18/98	915.3 ppm		

BALANCE   Nitrogen

PREVIOUS CERTIFICATION DATES: None

REFERENCE STANDARDS

COMPONENT	SRM/NTRM#	CYLINDER#	CONCENTRATION
Carbon Monoxide	NTRM-81681	CC55773	994 ppm

INSTRUMENTATION

COMPONENT	MAKE/MODEL	SERIAL #	DETECTOR	CALIBRATION DATE(S)
Carbon Monoxide	Horiba VIA-510	570423011	NDIR	7/30/98

THIS STANDARD WAS CERTIFIED ACCORDING TO THE EPA PROTOCOL PROCEDURES.
DO NOT USE THIS STANDARD IF THE CYLINDER PRESSURE IS LESS THAN 150 PSIG.

ANALYST: _____   DATE: _____8/18/98_____
          FRED PIKULA

SPECTRA GASES INC.

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Shipped From: 80 Industrial Drive • Alpha, NJ 08865

CERTIFICATE OF ANALYSIS

EPA PROTOCOL MIXTURE
PROCEDURE # : G2

CUSTOMER:	ETS, INC
SGI ORDER # :	135096
ITEM# :	3
P.O.# :	6873

CYLINDER # :	CC75430
CYLINDER PRES:	2000 PSIG
CGA OUTLET:	350

CERTIFICATION DATE: 8/18/98
EXPIRATION DATE: 8/18/2001

CERTIFICATION HISTORY

COMPONENT	DATE OF ASSAY	MEAN CONCENTRATION	CERTIFIED CONCENTRATION	ANALYTICAL ACCURACY
Carbon Monoxide	8/11/98	5962 ppm	5971 ppm	+/- 1%
	8/18/98	5979 ppm		

BALANCE   Nitrogen

PREVIOUS CERTIFICATION DATES: None

REFERENCE STANDARDS

COMPONENT	SRM/NTRM#	CYLINDER#	CONCENTRATION
Carbon Monoxide	NTRM–81681	CC55773	994 ppm

INSTRUMENTATION

COMPONENT	MAKE/MODEL	SERIAL #	DETECTOR	CALIBRATION DATE(S)
Carbon Monoxide	Horiba VIA-510	570423011	NDIR	7/30/98

THIS STANDARD WAS CERTIFIED ACCORDING TO THE EPA PROTOCOL PROCEDURES.

DO NOT USE THIS STANDARD IF THE CYLINDER PRESSURE IS LESS THAN 150 PSIG.

ANALYST: _____   DATE: 8/18/98
         FRED PIKULA

SPECTRA GASES INC.

3434 Route 22 West • Branchburg, NJ 08876 USA Tel.: (908) 252-9300 • (800) 932-0624 • Fax: (908) 252-0811
Shipped From: 80 Industrial Drive • Alpha, NJ 08865

5903

CERTIFICATE OF ANALYSIS

EPA PROTOCOL MIXTURE
PROCEDURE # : G2

CUSTOMER: ETS, INC
SGI ORDER # :   135096
ITEM# :   2
P.O.# :   6873

CYLINDER # :   CC53292
CYLINDER PRES: 2000 PSIG
CGA OUTLET: 350

CERTIFICATION DATE: 8/18/98
EXPIRATION DATE: 8/18/2001

CERTIFICATION HISTORY

COMPONENT	DATE OF ASSAY	MEAN CONCENTRATION	CERTIFIED CONCENTRATION	ANALYTICAL ACCURACY
Carbon Monoxide	8/11/98	2999 ppm	3005 ppm	+/- 1%
	8/18/98	3011 ppm		

BALANCE   Nitrogen

PREVIOUS CERTIFICATION DATES: None

REFERENCE STANDARDS

COMPONENT	SRM/NTRM#	CYLINDER#	CONCENTRATION
Carbon Monoxide	NTRM-81681	CC55773	994 ppm

INSTRUMENTATION

COMPONENT	MAKE/MODEL	SERIAL #	DETECTOR	CALIBRATION DATE(S)
Carbon Monoxide	Horiba VIA-510	570423011	NDIR	7/30/98

THIS STANDARD WAS CERTIFIED ACCORDING TO THE EPA PROTOCOL PROCEDURES.
DO NOT USE THIS STANDARD IF THE CYLINDER PRESSURE IS LESS THAN 150 PSIG.

ANALYST: _____   DATE: _____ 8/18/98
         FRED PIKULA

SPECTRA GASES INC.

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Shipped From: 80 Industrial Drive • Alpha, NJ 08865

CERTIFICATE OF ANALYSIS

EPA PROTOCOL MIXTURE
PROCEDURE # :   G2

CUSTOMER:	ETS, INC
SGI ORDER # :	144039
ITEM# :	1
P.O.# :	7275

CYLINDER # :	CC109915
CYLINDER PRES:	2000 PSIG
CGA OUTLET:	350

CERTIFICATION DATE: 7/6/99
EXPIRATION DATE: 7/6/2002

CERTIFICATION HISTORY

COMPONENT	DATE OF ASSAY	MEAN CONCENTRATION	CERTIFIED CONCENTRATION	ANALYTICAL ACCURACY
Carbon Monoxide	6/29/99	1813 ppm	1809 ppm	+/- 1%
	7/6/99	1804 ppm		
			--	

BALANCE   Nitrogen

PREVIOUS CERTIFICATION DATES: None

REFERENCE STANDARDS

COMPONENT	SRM/NTRM#	CYLINDER#	CONCENTRATION
Carbon Monoxide	NTRM-81681	CC55773	994 ppm

INSTRUMENTATION

COMPONENT	MAKE/MODEL	SERIAL #	DETECTOR	CALIBRATION DATE(S)
Carbon Monoxide	Horiba VIA-510	570423011	NDIR	6/28/99

THIS STANDARD WAS CERTIFIED ACCORDING TO THE EPA PROTOCOL PROCEDURES.
DO NOT USE THIS STANDARD IF THE CYLINDER PRESSURE IS LESS THAN 150 PSIG.

ANALYST: _____
FRED PIKULA

DATE: _____ 7/6/99 _____

Scott Specialty Gases

CERTIFICATE OF ANALYSIS: EPA PROTOCOL GAS

Customer	Assay Laboratory	
CLEAN AIR ENGINEERING	Scott Specialty Gases, Inc	Purchase Order : 18566-71-65000
ATTN DON ALLEN	1290 Combermere	Scott Project # : 543076
500 W WOOD STREET	Troy, MI 48083	
PALATINE, IL 60067		

ANALYTICAL INFORMATION

This certification was performed according to EPA Traceability Protocol For Assay and Certification of Gaseous Calibration Standards; Procedure G1; September, 1993.

Cylinder Number : AAL9476	Certificate Date : 4/7/99	Expiration Date : 4/7/2002
Cylinder Pressure + : 1900 psig	Previous Certificate Date : None	

ANALYZED CYLINDER

Components	Certified Concentration	Analytical Uncertainty*
Carbon Dioxide	6.13 %	±1% NIST Directly Traceable
Oxygen	14.2 %	±1% NIST Directly Traceable

Balance Gas: Nitrogen

+Do not use when cylinder pressure is below 150 psig.
*Analytical accuracy is inclusive of usual known error sources which at least include precision of the measurement processes.

REFERENCE STANDARD

Type	Expiration Date	Cylinder Number	Concentration
NTRM18000	4/12/2001	ALM047394	17.95 % Carbon Dioxide in Nitrogen
NTRM2659	12/1/2001	ALM065379	20.92 % Oxygen in Nitrogen

INSTRUMENTATION

Instrument/Model/Serial #	Last Date Calibrated	Analytical Principle
CO2: Horiba/OPE-135	4/7/99	Non-dipersive Infrared
Horiba	4/7/99	Paramagnetic

ANALYZER READINGS   (Z=Zero Gas R=Reference Gas T=Test Gas r=Correlation Coefficient)

Components	First Triad Analysis	Second Triad Analysis	Calibration Curve
Carbon Dioxide	Date: 4/7/99 Response Units: mv Z1=0.00 R1=90.20 T1=45.20 R2=90.20 Z2=0.00 T2=45.20 Z3=0.00 T3=45.20 R3=90.20 Avg. Conc. of Cust. Cyl. 6.13 %		Concentration=A+Bx+Cx²+Dx³+Ex⁴ r=1.00000 NTRM18000 Constants: A=-0.004980876 B=0.115273700 C=-0.000038791 D=0.000010886 E=0.000000000
Oxygen	Date: 4/7/99 Response Units: mv Z1=0.00 R1=120.00 T1=68.50 R2=120.00 Z2=0.00 T2=68.50 Z3=0.00 T3=68.50 R3=120.00 Avg. Conc. of Cust. Cyl. 14.2 %		Concentration=A+Bx+Cx²+Dx³+Ex⁴ r=1.00000 NTRM2659 Constants: A=-0.021996850 B=0.213390800 C=-0.000258055 D=0.000001812 E=0.000000000

Special Notes

Cylinder

Analyst

Scott Specialty Gases

1290 COMBERMERE STREET, TROY, MI 48083   Phone : (248) 589-2950   Fax : (248) 589-2134

CERTIFICATE OF ANALYSIS: EPA PROTOCOL GAS

Customer	Assay Laboratory	
CLEAN AIR ENGINEERING	Scott Specialty Gases, Inc	**Purchase Order :** 18373-75-65000
ATTN DON ALLEN	1290 Combermere	**Scott Project # :** 539848
500 W WOOD STREET	Troy, MI 48083	
PALATINE, IL 60067		

ANALYTICAL INFORMATION

This certification was performed according to EPA Traceability Protocol For Assay and Certification of Gaseous Calibration Standards; Procedure G1; September, 1993.

Cylinder Number : ALM008858   **Certificate Date :** 2/8/99   **Expiration Date :** 2/8/2002

Cylinder Pressure + : 1900 psig   **Previous Certificate Date :** None

ANALYZED CYLINDER

Components	Certified Concentration	Analytical Uncertainty*
Carbon Monoxide	467.0 ppm	±1% NIST Directly Traceable

Balance Gas: Nitrogen

+Do not use when cylinder pressure is below 150 psig.
*Analytical accuracy is inclusive of usual known error sources which at least include precision of the measurement processes.

REFERENCE STANDARD

Type	Expiration Date	Cylinder Number	Concentration
NTRM 1681	8/1/2002	ALM024833	966.1 ppm Carbon Monoxide in Nitrogen

INSTRUMENTATION

Instrument/Model/Serial #	Last Date Calibrated	Analytical Principle
CO: Horiba/OPE-135/565607092	2/8/99	Non-dispersive Infrared

ANALYZER READINGS   (Z=Zero Gas R=Reference Gas T=Test Gas r=Correlation Coefficient)

Components	First Triad Analysis			Second Triad Analysis			Calibration Curve	
Carbon Monoxide	Date: 2/1/99	Response Units: mv		Date: 2/8/99	Response Units: mv		Concentration=A+Bx+Cx^2+Dx^3+Ex^4	
	Z1=0.00	R1=100.00	T1=58.40	Z1=0.00	R1=100.00	T1=58.40	r=1.00000	NTRM 1681
	R2=100.00	Z2=0.00	T2=58.60	R2=100.00	Z2=0.00	T2=58.40	Constants:	A=0.411285000
	Z3=0.00	T3=58.40	R3=100.00	Z3=0.00	T3=58.40	R3=100.00	B=0.983850000	C=0.003370827
	Avg. Conc. of Cust. Cyl. 467.3 ppm			Avg. Conc. of Cust. Cyl. 466.7 ppm			D=0.000232584	E=0.000000000

Special Notes

Mail

Analyst

L-63

APPENDIX M

Process Field Data Sheets

M-1
Process Data Summary Tables

Table M-1
THC, O₂, Moisture, and Feed Rate Process Data
MSD Emission Test Program
No Runs
July 19, 1999

| Hour | Total Hydrocarbons (ppm) | | | Oxygen (%) | H₂O (%) | Sludge Feed (dry tons/hr) |
| | Uncorrected | Corrected (7% O2, dry) | | | | |
	Hourly Average	Hourly Average	Rolling Average			
0:00	45.8	81.5	89.3	12.8	3.1	1.80
1:00	40.7	72.3	76.2	12.8	3.0	1.79
2:00	43.3	68.6	74.1	11.5	3.0	1.78
3:00	43.4	72.6	71.2	12.4	3.0	1.78
4:00	38.2	66.3	69.2	12.6	3.0	1.78
5:00	41.2	72.9	70.6	12.8	3.0	1.78
6:00	46.4	84.8	74.7	13.1	2.9	1.80
7:00	46.1	80.2	79.3	12.7	2.9	1.79
8:00	52.6	92.7	85.9	12.8	2.9	1.78
9:00	45.8	83.1	85.3	12.7	2.9	1.78
10:00	37.0	57.8	77.9	11.7	3.1	1.79
11:00	28.2	45.9	62.3	12.1	2.9	1.43
12:00	21.7	40.6	48.1	13.3	3.1	1.16
13:00	22.0	46.7	44.4	14.2	3.2	1.58
14:00	36.8	65.8	51.1	12.9	3.0	1.78
15:00	49.9	90.9	67.8	13.0	3.0	1.78
16:00	55.5	97.7	84.8	12.8	3.0	1.79
17:00	35.2	53.4	80.7	11.5	3.1	1.59
18:00	44.2	60.9	70.7	9.6	3.3	1.27
19:00	14.4	26.9	47.1	13.3	3.1	1.55
20:00	28.8	53.0	47.0	12.9	3.0	1.80
21:00	48.2	89.1	56.3	13.2	3.0	1.87
22:00	52.8	78.4	73.5	11.7	3.1	1.87
23:00	43.5	72.4	79.9	12.2	3.1	1.76
Average	40.1	68.9		12.5	3.0	1.70

Set up day no tests

Table M-1
THC, O_2, Moisture, and Feed Rate Process Data
MSD Emission Test Program
Runs 1 and 2
July 20, 1999

Hour	Total Hydrocarbons (ppm)			Oxygen (%)	H_2O (%)	Sludge Feed (dry tons/hr)
	Uncorrected	Corrected (7% O2, dry)				
	Hourly Average	Hourly Average	Rolling Average			
0:00	23.6	38.1	62.9	12.0	3.1	1.72
1:00	22.6	48.3	52.9	14.3	3.1	1.72
2:00	26.5	40.6	42.3	10.8	3.1	1.72
3:00	21.0	38.6	42.5	13.1	3.1	1.72
4:00	35.2	63.9	47.7	13.0	3.1	1.72
5:00	39.4	69.4	57.3	12.8	3.0	1.72
6:00	39.7	67.7	67.0	12.5	3.0	1.72
7:00	38.3	63.3	66.8	12.3	3.0	1.72
8:00	40.1	69.0	66.7	12.6	3.0	1.72
9:00	39.1	64.6	65.7	12.3	3.0	1.72
10:00	37.7	66.7	66.8	12.8	3.0	1.72
11:00	34.1	54.1	61.8	11.8	3.1	1.72
12:00	28.6	46.4	55.7	12.0	3.1	1.72
13:00	26.5	44.7	48.4	12.4	3.1	1.72
14:00	30.0	49.4	46.8	12.2	3.1	1.72
15:00	37.4	66.8	53.6	12.9	3.1	1.72
16:00	42.0	71.4	62.5	12.5	3.1	1.72
17:00	38.5	67.7	68.6	12.7	3.1	1.72
18:00	41.6	63.2	67.4	10.8	3.1	1.72
19:00	41.9	75.5	68.8	13.0	3.1	1.72
20:00	42.8	74.8	71.1	12.7	3.1	1.72
21:00	43.4	78.2	76.2	13.0	3.1	1.74
22:00	40.3	67.5	73.5	12.3	3.1	1.81
23:00	39.9	63.8	69.9	12.0	3.1	1.81
Run 1 Average		57.9		12.2	3.1	1.72
Run 2 Average		70.6		12.5	3.1	1.74

Shaded cells include test run data

Table M-1
THC, O₂, Moisture, and Feed Rate Process Data
MSD Emission Test Program
Run 3
July 21, 1999

Hour	Total Hydrocarbons (ppm)			Oxygen (%)	H₂O (%)	Sludge Feed (dry tons/hr)
	Uncorrected	Corrected (7% O2, dry)				
	Hourly Average	Hourly Average	Rolling Average			
0:00	34.7	57.9	63.1	12.3	3.1	1.45
1:00	45.3	77.6	66.4	12.6	3.0	1.45
2:00	43.6	67.5	67.7	11.3	3.0	1.45
3:00	35.5	58.1	67.7	12.2	3.0	1.45
4:00	40.9	70.5	65.4	12.6	3.0	1.45
5:00	44.8	77.8	68.8	12.7	3.0	1.45
6:00	45.6	78.7	75.7	12.6	3.0	1.45
7:00	39.2	63.6	73.4	12.1	3.0	1.45
8:00	36.3	61.7	68.0	12.5	3.0	1.44
9:00	42.7	84.5	69.9	13.7	3.0	1.45
10:00	45.1	94.8	80.3	14.1	3.1	1.45
11:00	41.6	73.3	84.2	12.8	3.2	1.45
12:00	47.9	72.6	80.2	11.6	3.2	1.45
13:00	27.2	44.7	63.5	12.2	3.2	1.45
14:00	27.1	41.3	52.9	11.4	3.3	1.45
15:00	22.6	36.8	41.0	12.1	3.2	1.45
16:00	20.4	31.3	36.5	11.5	3.3	1.45
17:00	22.7	38.8	35.7	12.5	3.2	1.45
18:00	18.2	24.9	31.7	9.4	3.3	1.44
19:00	15.8	24.1	29.3	11.5	3.3	1.41
20:00	16.7	29.2	26.1	12.7	3.2	1.39
21:00	22.4	38.9	30.7	12.6	3.2	1.39
22:00	18.4	32.4	33.5	12.7	3.2	1.39
23:00	25.9	45.8	39.0	12.8	3.2	1.39
Run 3 Average		54.2		12.3	3.2	1.45

Shaded cells include test run data

Table M-1
THC, O₂, Moisture, and Feed Rate Process Data
MSD Emission Test Program
Run4
July 22, 1999

| Hour | Total Hydrocarbons (ppm) | | | Oxygen (%) | H₂O (%) | Sludge Feed (dry tons/hr) |
| | Uncorrected | Corrected (7% O2, dry) | | | | |
	Hourly Average	Hourly Average	Rolling Average			
0:00	21.0	37.7	38.6	12.9	3.2	1.55
1:00	28.0	48.7	44.1	12.6	3.2	1.53
2:00	21.0	34.4	40.3	10.9	3.2	1.53
3:00	29.7	51.6	44.9	12.6	3.2	1.53
4:00	20.6	35.8	40.6	12.7	3.1	1.53
5:00	18.8	31.7	39.7	12.4	3.1	1.53
6:00	21.6	42.5	36.6	13.7	3.1	1.53
7:00	37.7	80.1	51.4	14.2	3.2	1.53
8:00	32.5	57.3	60.0	12.7	3.2	1.53
9:00	20.4	37.8	58.4	13.2	3.2	1.53
10:00	20.1	34.6	43.2	12.6	3.2	1.53
11:00	20.8	36.3	36.2	12.7	3.3	1.53
12:00	18.5	31.4	34.1	12.5	3.3	1.53
13:00	19.2	33.3	33.7	12.7	3.3	1.53
14:00	18.2	30.6	31.8	12.4	3.3	1.53
15:00	22.6	38.8	34.2	12.6	3.3	1.53
16:00	24.7	39.4	36.3	11.9	3.3	1.53
17:00	18.9	31.4	36.5	12.3	3.3	1.53
18:00	23.7	33.1	34.6	9.8	3.4	1.53
19:00	18.6	31.6	32.0	12.5	3.3	1.51
20:00	23.4	39.6	34.7	12.4	3.3	1.52
21:00	23.3	37.1	36.1	11.9	3.3	1.54
22:00	22.9	39.2	38.6	12.6	3.3	1.57
23:00	28.1	48.4	41.6	12.6	3.2	1.58
Run 4 Average		37.5		12.6	3.3	1.53

Shaded cells include test run data

M-2
MSD Daily Data Reports

Metropolitan Sewer District of Greater Cincinnati and Hamilton County
Mill Creek Waste Water Treatment Plant

Date of Report
7/19/1999

Incinerator #6 "Daily" Report

Hour	Uncorr. THC (ppm)	CEM Oxygen (%)	Moist. H2O (%)	Corr. THC (ppm)	Rolling C. THC (ppm)	Sludge Feed (wet lb/hr)	Sludge Feed (dry lb/hr)	Accum. Sludge (dry tons)	LOWEST STATUS	HIGHEST STATUS	Report Event
0:00	45.8	12.81	3.09	81.51	89.29	15426	3604	1.80	BURN	BURN	NO
1:00	40.7	12.85	3.02	72.30	76.18	15345	3585	3.59	BURN	BURN	NO
2:00	43.3	11.48	2.98	68.61	74.14	15245	3561	5.37	BURN	BURN	NO
3:00	43.4	12.38	3.00	72.63	71.18	15245	3561	7.16	BURN	BURN	NO
4:00	38.2	12.65	2.97	66.26	69.17	15245	3561	8.94	BURN	BURN	NO
5:00	41.2	12.85	2.95	72.93	70.60	15245	3561	10.72	BURN	BURN	NO
6:00	48.4	13.10	2.92	84.81	74.67	15384	3594	12.51	BURN	BURN	NO
7:00	46.1	12.70	2.92	80.21	79.32	15366	3589	14.31	BURN	BURN	NO
8:00	52.6	12.76	2.89	92.71	85.91	15245	3561	16.09	BURN	BURN	NO
9:00	45.8	12.68	2.91	83.09	85.34	15245	3561	17.87	BURN	BURN	NO
10:00	37.0	11.73	3.05	57.84	77.88	15329	3581	19.66	BURN	BURN	NO
11:00	28.2	12.13	2.93	45.85	62.26	12211	2852	21.09	BURN	BURN	NO
12:00	21.7	13.34	3.09	40.60	48.10	9891	2311	22.24	BURN	BURN	NO
13:00	22.0	14.22	3.20	46.75	44.40	13506	3155	23.82	BURN	BURN	NO
14:00	36.8	12.93	3.01	65.84	51.06	15245	3561	25.60	BURN	BURN	NO
15:00	49.9	13.02	3.04	90.93	67.84	15245	3561	27.38	BURN	BURN	NO
16:00	55.5	12.80	3.02	97.74	84.84	15314	3577	29.17	BURN	BURN	NO
17:00	35.2	11.49	3.05	53.41	80.69	13645	3187	30.76	BURN	BURN	NO
18:00	44.2	9.59	3.28	60.95	70.70	10868	2539	32.03	BURN	BURN	NO
19:00	14.4	13.30	3.13	26.94	47.10	13288	3104	33.58	BURN	BURN	NO
20:00	28.8	12.94	3.02	52.98	46.96	15408	3599	35.38	BURN	BURN	NO
21:00	48.2	13.19	3.02	89.06	56.33	15971	3731	37.25	BURN	BURN	NO
22:00	52.8	11.70	3.12	78.39	73.48	15971	3731	39.11	BURN	BURN	NO
23:00	43.5	12.24	3.12	72.37	79.94	15079	3522	40.88	BURN	BURN	NO
	40.1	12.54	3.03	68.95	69.47	14582	3406	40.88			0

SludgeMultiplier = 0.234

*NOTE: FOR "YES" REPORT EVENT

O2 = HIGH OXYGEN VIOLATION   DP = LOW SCRUBBER DP VIOLATION
SQ = LOW SCRUBBER FLOW VIOLATION   OP = HIGH OPACITY VIOLATION

Print Date: 8/24/99
Print Time: 10:52 AM

Date of Report
7/19/1999

Incinerator #6 "Daily" Report

Hour	Fuel N. Gas (scfh)	Accum. N. Gas (cf)	Fuel Digester (scfm)	Accum. Digester (cf)	Fuel Oil (gpm)	Accum. Fuel Oil (gal)	Furnace Pressure (in.H2O)	Scrubber D.P. (in.H2O)	Flue Opacity (%)	Breech O2 (%)	Scrub Q GPM	Inc. Burn Hours (hr)
0:00	2903	2903	0	0			-0.51	28.45	4.0	5.3	1225	1
1:00	2732	5635	6	6			-0.50	28.13	3.0	4.2	1224	1
2:00	1990	7625	1030	1036			-0.51	28.15	3.0	4.0	1226	1
3:00	1437	9062	2615	3651			-0.50	28.05	3.0	3.7	1226	1
4:00	1201	10263	2340	5991			-0.50	28.18	3.0	4.1	1227	1
5:00	184	10447	6	5997			-0.50	28.08	3.0	4.5	1228	1
6:00	0	10447	12	6009			-0.50	28.00	3.0	5.6	1227	1
7:00	36	10483	30	6039			-0.50	28.03	3.0	3.8	1228	1
8:00	166	10649	0	6039			-0.50	28.05	3.0	5.1	1297	1
9:00	3756	14405	0	6039			-0.50	28.28	2.9	5.4	1352	1
10:00	2521	16926	6	6045			-0.50	28.50	3.5	2.8	1355	1
11:00	0	16926	6	6051			-0.50	28.13	2.7	5.7	1351	1
12:00	1756	18682	12	6063			-0.49	28.15	2.0	8.9	1347	1
13:00	3695	22377	1937	8000			-0.39	27.70	2.7	6.1	1338	1
14:00	271	22648	2548	10548			-0.30	27.08	3.0	5.2	1335	1
15:00	2	22650	676	11224			-0.31	26.85	2.6	5.5	1332	1
16:00	1665	24315	15	11239			-0.30	26.95	4.3	4.9	1332	1
17:00	3233	27548	406	11645			-0.30	27.30	3.0	3.4	1332	1
18:00	1468	29016	577	12222			-0.30	28.28	3.1	6.1	1331	1
19:00	4599	33615	17	12239			-0.31	27.33	3.0	5.1	1328	1
20:00	602	34217	0	12239			-0.30	27.08	3.0	4.8	1327	1
21:00	3556	37773	614	12853			-0.29	27.53	3.7	4.2	1327	1
22:00	3695	41468	1797	14650			-0.34	28.40	3.9	4.4	1325	1
23:00	3476	44944	1871	16521			-0.35	28.35	3.8	4.5	1323	1
	1873	44944	688	16521			-0.42	27.87	3.1	4.9	1298	24

*** N.I.B. = incinerator was not in burn mode.***

PROCESS OXYGEN DAILY (MANUAL) CALIBRATION APROX TIME: 09:07   BY: KC

Calibration Results of THC and O2 Analyzers					Time of Calibration
	Bottle conc. (pom)	Cylinder ID #	Zero (ppm)	Span (ppm)	8 : 15
THC	176	sx-34161	0.0	176.0	
O2	19.9	130	0.1	20.10	

Date of Report
7/19/1999

Incinerator #6 "Daily" Report

Hour	Afterb. Temp. (F)	Breech Temp. (F)	Hrth. 1 Temp. (F)	Hrth. 2 Temp. (F)	Hrth. 3 Temp. (F)	Hrth. 4 Temp. (F)	Hrth. 5 Temp. (F)	Hrth. 6 Temp. (F)	Hrth. 7 Temp. (F)	Hrth. 8 Temp. (F)	Hrth. 9 Temp. (F)
0:00	903	947	1136	1144	1502	1624	1405	1410	1016	703	218
1:00	873	930	1123	1140	1506	1626	1409	1403	1016	695	210
2:00	861	920	1108	1123	1484	1595	1408	1423	1015	712	210
3:00	877	945	1141	1158	1529	1644	1416	1405	1015	740	212
4:00	881	946	1140	1158	1526	1638	1404	1410	1015	700	208
5:00	865	921	1108	1127	1472	1576	1400	1430	1015	697	206
6:00	844	884	1071	1091	1371	1450	1404	1455	1015	733	208
7:00	856	920	1119	1139	1481	1590	1400	1426	1015	762	211
8:00	868	925	1109	1125	1426	1508	1401	1437	1015	736	210
9:00	957	942	1042	1054	1321	1398	1422	1511	1014	751	210
10:00	948	1029	1219	1236	1568	1672	1449	1444	1015	718	215
11:00	902	964	1194	1227	1514	1603	1417	1420	1016	669	208
12:00	931	1007	1246	1286	1580	1668	1394	1310	1014	647	207
13:00	915	990	1176	1202	1511	1605	1390	1271	1016	622	204
14:00	875	935	1132	1161	1532	1649	1382	1349	1015	636	210
15:00	836	875	1058	1078	1413	1509	1403	1430	1015	698	219
16:00	853	875	1015	1024	1260	1328	1418	1515	1015	769	226
17:00	931	974	1067	1079	1256	1320	1465	1583	1015	824	237
18:00	982	1087	1267	1289	1551	1622	1431	1399	1007	784	238
19:00	962	1012	1198	1233	1528	1642	1399	1289	965	719	206
20:00	906	928	1109	1140	1435	1563	1416	1429	1015	734	201
21:00	860	877	997	1003	1241	1317	1447	1488	1016	794	220
22:00	930	952	1046	1042	1272	1352	1495	1570	1014	831	264
23:00	944	971	1062	1063	1254	1339	1502	1587	1015	813	239
	898	948	1120	1138	1439	1535	1420	1433	1013	729	217

Date of Report
7/19/1999

Incinerator #6 "Daily" Report

			Scrubber			
	RANGE LIMIT =	26.0	inches H2O			
Minute=>	0	15	30	45	HrAvg	#<LIMIT
Hour						
0:00	28.7	28.4	28.4	28.3	28.45	0
1:00	28.3	28.1	28.1	28.0	28.13	0
2:00	28.0	28.1	28.3	28.2	28.15	0
3:00	28.0	28.0	28.0	28.2	28.05	0
4:00	28.2	28.1	28.2	28.2	28.18	0
5:00	28.0	28.1	28.1	28.1	28.08	0
6:00	27.9	28.1	28.0	28.0	28.00	0
7:00	28.1	28.0	28.0	28.0	28.03	0
8:00	28.1	28.1	28.0	28.0	28.05	0
9:00	28.2	28.1	28.2	28.6	28.28	0
10:00	29.3	28.4	28.2	28.1	28.50	0
11:00	28.2	28.3	28.1	27.9	28.13	0
12:00	27.8	28.3	28.2	28.3	28.15	0
13:00	28.3	28.0	27.4	27.1	27.70	0
14:00	27.0	27.0	27.3	27.0	27.08	0
15:00	26.7	26.9	27.1	26.7	26.85	0
16:00	26.7	26.4	27.3	27.4	26.95	0
17:00	27.2	27.2	27.3	27.5	27.30	0
18:00	29.9	28.8	27.3	27.1	28.28	0
19:00	27.2	27.3	27.3	27.5	27.33	0
20:00	27.3	27.0	26.9	27.1	27.08	0
21:00	27.3	27.0	27.6	28.2	27.53	0
22:00	28.3	28.5	28.4	28.4	28.40	0
23:00	28.3	28.4	28.3	28.4	28.35	0
					27.87	0

*** All values in brackets [ ] occured while incinerator was not in burn mode.***
*** N.I.B. == Incinerator was not in burn mode.***

Date of Report
7/19/1999

Incinerator #6 "Daily" Report

Minute=> Hour	0	6	12	18	24	Flue Gas Opacity (%) 30	36	42	48	54	HrAvg	#>20	#>60
0:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
1:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
2:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
3:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
4:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
5:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
6:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
7:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
8:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
9:00	3	3	3	3	3	3	3	3	3	2	2.9	0	0
10:00	3	5	5	4	3	3	3	3	3	3	3.5	0	0
11:00	3	3	3	3	3	3	3	2	2	2	2.7	0	0
12:00	2	2	2	2	2	2	2	2	2	2	2.0	0	0
13:00	2	2	2	3	3	3	3	3	3	3	2.7	0	0
14:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
15:00	3	3	3	3	3	2	2	2	2	3	2.6	0	0
16:00	3	3	3	2	17	3	3	3	3	3	4.3	0	0
17:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
18:00	3	4	3	3	3	3	3	3	3	3	3.1	0	0
19:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
20:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
21:00	4	4	3	4	4	4	4	4	3	3	3.7	0	0
22:00	5	4	3	3	4	4	4	4	4	4	3.9	0	0
23:00	4	4	3	3	4	4	4	4	4	4	3.8	0	0
	3.1	3.2	3.0	3.0	3.7	3.1	3.1	3.0	3.0	3.0	3.1	0	0

OPACITY DAILY AUTOMATIC CALIBRATION AT TIME: 16:27

Metropolitan Sewer District of Greater Cincinnati and Hamilton County
Mill Creek Waste Water Treatment Plant

Date of Report
7/20/1999

Incinerator #6 "Daily" Report

Hour	Uncorr. THC (ppm)	CEM Oxygen (%)	Moist. H2O (%)	Corr. THC (ppm)	Rolling C. THC (ppm)	Sludge Feed (wet lb/hr)	Sludge Feed (dry lb/hr)	Accum. Sludge (dry tons)	LOWEST STATUS	HIGHEST STATUS	Report Event
0:00	23.6	12.02	3.09	38.08	62.95	14156	3448	1.72	BURN	BURN	NO
1:00	22.6	14.28	3.12	48.29	52.91	14156	3448	3.45	BURN	BURN	NO
2:00	26.5	10.76	3.07	40.64	42.34	14156	3448	5.17	BURN	BURN	NO
3:00	21.0	13.06	3.06	38.56	42.50	14156	3448	6.90	BURN	BURN	NO
4:00	35.2	13.03	3.08	63.86	47.69	14156	3448	8.62	BURN	BURN	NO
5:00	39.4	12.79	3.02	69.39	57.27	14156	3448	10.35	BURN	BURN	NO
6:00	39.7	12.52	3.03	67.69	66.98	14156	3448	12.07	BURN	BURN	NO
7:00	38.3	12.26	3.03	63.35	66.81	14156	3448	13.79	BURN	BURN	NO
8:00	40.1	12.62	3.02	69.03	66.69	14156	3448	15.52	BURN	BURN	NO
9:00	39.1	12.25	3.05	64.63	65.67	14156	3448	17.24	BURN	BURN	NO
10:00	37.7	12.84	3.03	66.70	66.79	14156	3448	18.97	BURN	BURN	NO
11:00	34.1	11.83	3.10	54.08	61.81	14156	3448	20.69	BURN	BURN	NO
12:00	28.6	12.05	3.08	46.37	55.72	14156	3448	22.41	BURN	BURN	NO
13:00	26.5	12.37	3.08	44.69	48.38	14156	3448	24.14	BURN	BURN	NO
14:00	30.0	12.23	3.12	49.36	46.81	14156	3448	25.86	BURN	BURN	NO
15:00	37.4	12.92	3.12	66.81	53.62	14156	3448	27.59	BURN	BURN	NO
16:00	42.0	12.49	3.14	71.43	62.53	14156	3448	29.31	BURN	BURN	NO
17:00	38.5	12.74	3.12	67.69	68.64	14156	3448	31.04	BURN	BURN	NO
18:00	41.6	10.78	3.13	63.18	67.43	14156	3448	32.76	BURN	BURN	NO
19:00	41.9	12.99	3.13	75.48	68.78	14156	3448	34.48	BURN	BURN	NO
20:00	42.8	12.73	3.12	74.78	71.15	14156	3448	36.21	BURN	BURN	NO
21:00	43.4	12.97	3.12	78.24	76.17	14277	3478	37.95	BURN	BURN	NO
22:00	40.3	12.35	3.15	67.55	73.52	14882	3625	39.76	BURN	BURN	NO
23:00	39.9	11.97	3.14	63.78	69.86	14882	3625	41.57	BURN	BURN	NO
	35.4	12.45	3.09	60.57	60.96	14222	3464	41.57			0

SludgeMultiplier = 0.244

*NOTE: FOR "YES" REPORT EVENT

O2 = HIGH OXYGEN VIOLATION   DP = LOW SCRUBBER DP VIOLATION
SQ = LOW SCRUBBER FLOW VIOLATION   OP = HIGH OPACITY VIOLATION

Print Date: 8/24/99
Print Time: 10:51 AM

M-12

Metropolitan Sewer District of Greater Cincinnati and Hamilton County
Mill Creek Waste Water Treatment Plant

Date of Report
7/20/1999

Incinerator #6 "Daily" Report

Hour	Fuel N. Gas (scfh)	Accum. N. Gas (cf)	Fuel Digester (scfm)	Accum. Digester (cf)	Fuel Oil (gpm)	Accum. Fuel Oil (gal)	Furnace Pressure (in.H2O)	Scrubber D.P. (in.H2O)	Flue Opacity (%)	Breech O2 (%)	Scrub Q GPM	Inc. Burn Hours (hr)
0:00	2477	2477	2084	2084			-0.35	28.23	3.5	5	1322	1
1:00	4035	6512	2397	4481			-0.35	28.25	4.0	5.5	1320	1
2:00	4802	11314	2861	7342			-0.35	28.08	3.7	5.2	1317	1
3:00	2302	13616	299	7641			-0.35	28.08	4.0	6.2	1313	1
4:00	2549	16165	0	7641			-0.35	28.00	4.0	5.5	1311	1
5:00	1627	17792	1353	8994			-0.35	28.03	4.0	5.3	1310	1
6:00	1369	19161	2002	10996			-0.35	28.03	4.0	5.0	1310	1
7:00	738	19899	2491	13487			-0.35	27.93	4.0	4.8	1308	1
8:00	630	20529	2964	16451			-0.35	28.00	4.0	4.9	1307	1
9:00	629	21158	3259	19710			-0.35	28.05	3.3	4.6	1310	1
10:00	2044	23202	3231	22941			-0.35	28.10	3.6	5.4	1308	1
11:00	5402	28604	2710	25651			-0.35	28.15	3.0	3.5	1306	1
12:00	3088	31692	2293	27944			-0.36	28.08	3.0	4.2	1303	1
13:00	3128	34820	1426	29370			-0.35	28.08	3.0	4.5	1294	1
14:00	2221	37041	0	29370			-0.35	28.03	3.2	4.2	1288	1
15:00	256	37297	19	29389			-0.35	27.98	4.0	4.5	1288	1
16:00	179	37476	564	29953			-0.35	27.95	5.2	4.5	1289	1
17:00	31	37507	38	29991			-0.36	28.00	4.0	4.5	1290	1
18:00	0	37507	0	29991			-0.35	28.00	4.0	4.4	1290	1
19:00	0	37507	0	29991			-0.35	28.00	4.0	4.7	1288	1
20:00	0	37507	0	29991			-0.35	27.88	4.0	4.9	1287	1
21:00	1202	38709	658	30649			-0.36	27.95	3.9	4.8	1286	1
22:00	2350	41059	13	30662			-0.35	27.83	3.7	4.5	1289	1
23:00	2033	43092	15	30677			-0.35	27.85	4.0	3.9	1293	1
	1796	43092	1278	30677			-0.35	28.02	3.8	4.8	1301	24

*** N.I.B. == Incinerator was not in burn mode.***

PROCESS OXYGEN DAILY (MANUAL) CALIBRATION APROX TIME: 08:25   BY: KC

Calibration Results of THC and O2 Analyzers					Time of Calibration
	Bottle conc. (ppm)	Cylinder ID #	Zero (ppm)	Span (ppm)	8 : 15
THC	176	sx-34161	0.0	175.6	
O2	19.9	130	0.1	20.05	

Print Date: 8/24/99
Print Time: 10:51 AM

Date of Report
7/20/1999

Incinerator #6 "Daily" Report

Hour	Afterb. Temp. (F)	Breech Temp. (F)	Hrth. 1 Temp. (F)	Hrth. 2 Temp. (F)	Hrth. 3 Temp. (F)	Hrth. 4 Temp. (F)	Hrth. 5 Temp. (F)	Hrth. 6 Temp. (F)	Hrth. 7 Temp. (F)	Hrth. 8 Temp. (F)	Hrth. 9 Temp. (F)
0:00	985	1030	1184	1195	1476	1593	1442	1440	994	746	221
1:00	922	955	1117	1131	1442	1589	1339	1322	930	651	212
2:00	959	988	1140	1152	1503	1640	1430	1432	1013	732	212
3:00	938	945	1096	1103	1388	1484	1447	1453	1013	732	209
4:00	905	926	1079	1085	1329	1382	1439	1458	1016	733	209
5:00	902	925	1081	1089	1293	1334	1433	1469	1015	726	211
6:00	908	938	1099	1106	1302	1348	1434	1479	1015	733	211
7:00	917	951	1115	1123	1325	1374	1436	1482	1015	741	212
8:00	903	931	1081	1087	1296	1343	1439	1491	1015	726	209
9:00	917	952	1109	1116	1325	1375	1438	1488	1015	741	209
10:00	908	937	1102	1103	1273	1324	1425	1478	1015	730	208
11:00	943	998	1160	1164	1431	1513	1434	1440	1014	722	206
12:00	951	995	1151	1162	1411	1469	1447	1450	1032	677	203
13:00	945	985	1142	1156	1408	1500	1446	1443	1040	655	202
14:00	941	980	1134	1146	1398	1467	1458	1470	1040	654	201
15:00	903	931	1076	1088	1341	1422	1472	1523	1040	653	201
16:00	906	938	1086	1097	1329	1399	1468	1528	1040	661	203
17:00	899	931	1080	1094	1339	1428	1468	1526	1040	650	202
18:00	903	939	1097	1111	1362	1448	1463	1519	1040	657	202
19:00	886	915	1061	1075	1316	1392	1468	1528	1040	646	200
20:00	885	915	1063	1076	1314	1393	1457	1516	1040	655	200
21:00	882	913	1061	1070	1303	1379	1455	1519	1040	651	200
22:00	908	947	1102	1111	1337	1403	1450	1508	1040	668	200
23:00	921	965	1122	1132	1377	1437	1451	1489	1040	673	200
	918	951	1106	1116	1359	1435	1443	1477	1023	692	206

Date of Report
7/20/1999

Incinerator #6 "Daily" Report

			Scrubber			
	RANGE LIMIT =	26.0	inches H2O			
Minute=>	0	15	30	45	HrAvg	#<LIMIT
Hour						
0:00	28.4	28.1	28.2	28.2	28.23	0
1:00	28.2	28.3	28.3	28.2	28.25	0
2:00	28.0	28.0	28.0	28.3	28.08	0
3:00	28.0	28.2	28.0	28.1	28.08	0
4:00	28.1	28.2	27.9	27.8	28.00	0
5:00	27.9	28.0	28.1	28.1	28.03	0
6:00	27.9	28.0	28.1	28.1	28.03	0
7:00	27.9	27.9	27.9	28.0	27.93	0
8:00	27.9	27.9	28.0	28.2	28.00	0
9:00	28.1	28.0	28.1	28.0	28.05	0
10:00	27.9	28.2	28.2	28.1	28.10	0
11:00	28.3	28.1	28.1	28.1	28.15	0
12:00	28.0	28.1	28.2	28.0	28.08	0
13:00	28.0	28.1	28.1	28.1	28.08	0
14:00	28.2	28.1	27.9	27.9	28.03	0
15:00	27.9	28.0	28.0	28.0	27.98	0
16:00	27.9	27.9	28.1	27.9	27.95	0
17:00	27.9	28.0	28.0	28.1	28.00	0
18:00	28.0	27.9	28.0	28.1	28.00	0
19:00	28.1	28.1	27.9	27.9	28.00	0
20:00	27.9	27.9	27.9	27.8	27.88	0
21:00	27.8	27.9	27.9	28.2	27.95	0
22:00	27.7	27.8	28.0	28.0	27.83	0
23:00	27.8	27.8	27.9	27.9	27.85	0
					28.02	0

*** All values in brackets [] occured while incinerator was not in burn mode.***

*** N.I.B. == Incinerator was not in burn mode.***

Metropolitan Sewer District of Greater Cincinnati and Hamilton County
Mill Creek Waste Water Treatment Plant

Date of Report
7/20/1999

Incinerator #6 "Daily" Report

						Flue Gas Opacity (%)							
Minute=> Hour	0	6	12	18	24	30	36	42	48	54	HrAvg	#>20	#>60
0:00	4	3	3	3	3	3	4	4	4	4	3.5	0	0
1:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
2:00	4	4	4	4	4	4	4	3	3	3	3.7	0	0
3:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
4:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
5:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
6:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
7:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
8:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
9:00	4	4	3	3	3	3	3	3	3	4	3.3	0	0
10:00	4	4	4	4	4	4	3	3	3	3	3.6	0	0
11:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
12:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
13:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
14:00	3	3	3	3	3	3	3	3	4	4	3.2	0	0
15:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
16:00	4	4	4	3	17	4	4	4	4	4	5.2	0	0
17:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
18:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
19:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
20:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
21:00	4	4	4	4	4	4	4	4	4	3	3.9	0	0
22:00	3	3	3	4	4	4	4	4	4	4	3.7	0	0
23:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
	3.8	3.8	3.7	3.7	4.3	3.8	3.8	3.7	3.8	3.8	3.8	0	0

OPACITY DAILY AUTOMATIC CALIBRATION AT TIME: 16:27

Date of Report
7/21/1999

Incinerator #6 "Daily" Report

Hour	Uncorr. THC (ppm)	CEM Oxygen (%)	Moist. H2O (%)	Corr. THC (ppm)	Rolling C. THC (ppm)	Sludge Feed (wet lb/hr)	Sludge Feed (dry lb/hr)	Accum. Sludge (dry tons)	LOWEST STATUS	HIGHEST STATUS	Report Event
0:00	34.7	12.27	3.07	57.88	63.07	14882	2893	1.45	BURN	BURN	NO
1:00	45.3	12.56	3.05	77.59	66.42	14882	2893	2.89	BURN	BURN	NO
2:00	43.6	11.30	3.04	67.52	67.66	14882	2893	4.34	BURN	BURN	NO
3:00	35.5	12.18	3.04	58.12	67.75	14882	2893	5.79	BURN	B'JRN	NO
4:00	40.9	12.63	3.02	70.51	65.39	14882	2893	7.23	BURN	BURN	NO
5:00	44.8	12.70	3.02	77.84	68.83	14882	2893	8.68	BURN	BURN	NO
6:00	45.6	12.62	3.02	78.69	75.68	14882	2893	10.13	BURN	BURN	NO
7:00	39.2	12.11	3.03	63.64	73.39	14882	2893	11.57	BURN	BURN	NO
8:00	36.3	12.51	3.01	61.72	68.02	14828	2883	13.01	BURN	BURN	NO
9:00	42.7	13.72	3.04	84.47	69.94	14882	2893	14.46	BURN	BURN	NO
10:00	45.1	14.11	3.08	94.75	80.31	14882	2893	15.91	BURN	BURN	NO
11:00	41.6	12.75	3.15	73.28	84.16	14882	2893	17.35	BURN	BURN	NO
12:00	47.9	11.56	3.21	72.55	80.19	14882	2893	18.80	BURN	BURN	NO
13:00	27.2	12.20	3.21	44.73	63.52	14882	2893	20.25	BURN	BURN	NO
14:00	27.1	11.44	3.25	41.33	52.87	14882	2893	21.69	BURN	BURN	NO
15:00	22.6	12.12	3.25	36.83	40.97	14882	2893	23.14	BURN	BURN	NO
16:00	20.4	11.53	3.30	31.33	36.50	14882	2893	24.59	BURN	BURN	NO
17:00	22.7	12.52	3.25	38.80	35.66	14882	2893	26.03	BURN	BURN	NO
18:00	18.2	9.43	3.31	24.90	31.68	14792	2876	27.47	BURN	BURN	NO
19:00	15.8	11.49	3.27	24.12	29.27	14556	2830	28.88	BURN	BURN	NO
20:00	16.7	12.73	3.23	29.22	26.08	14338	2787	30.28	BURN	BURN	NO
21:00	22.4	12.63	3.23	38.89	30.74	14338	2787	31.67	BURN	BURN	NO
22:00	18.4	12.74	3.23	32.40	33.50	14338	2787	33.07	BURN	BURN	NO
23:00	25.9	12.79	3.23	45.83	39.04	14338	2787	34.46	BURN	BURN	NO
	32.5	12.28	3.15	55.29	56.28	14772	2872	34.46			0

SludgeMultiplier =   0.194

*NOTE: FOR "YES" REPORT EVENT

O2 = HIGH OXYGEN VIOLATION   DP = LOW SCRUBBER DP VIOLATION
SQ = LOW SCRUBBER FLOW VIOLATION   OP = HIGH OPACITY VIOLATION

Print Date: 8/24/99
Print Time: 10:50 AM

Metropolitan Sewer District of Greater Cincinnati and Hamilton County
Mill Creek Waste Water Treatment Plant

Date of Report
7/21/1999

Incinerator #6 "Daily" Report

Hour	Fuel N. Gas (scfh)	Accum. N. Gas (cf)	Fuel Digester (scfm)	Accum. Digester (cf)	Fuel Oil (gpm)	Accum. Fuel Oil (gal)	Furnace Pressure (in.H2O)	Scrubber D.P. (in.H2O)	Flue Opacity (%)	Breech O2 (%)	Scrub Q GPM	Inc. Burn Hours (hr)
0:00	374	374	384	384			-0.35	27.65	4.0	4.4	1296	1
1:00	0	374	2077	2461			-0.35	27.68	4.0	4.5	1293	1
2:00	580	954	1662	4123			-0.35	27.78	4.0	4.1	1294	1
3:00	1911	2865	12	4135			-0.35	27.88	4.0	4.4	1294	1
4:00	7	2872	356	4491			-0.35	27.70	4.0	4.6	1293	1
5:00	0	2872	289	4780			-0.35	27.73	4.0	4.7	1300	1
6:00	215	3087	1362	6142			-0.35	27.85	4.0	4.5	1304	1
7:00	946	4033	1708	7850			-0.35	27.88	4.0	4.2	1301	1
8:00	163	4196	1562	9412			-0.35	27.83	4.0	4.9	1306	1
9:00	1275	5471	1273	10685			-0.35	27.85	4.4	5.9	1313	1
10:00	2337	7808	279	10964			-0.35	27.88	4.6	6.1	1314	1
11:00	4195	12003	0	10964			-0.35	28.30	3.9	5.7	1312	1
12:00	4802	16805	373	11337			-0.35	28.20	3.0	4.5	1317	1
13:00	7192	23997	13	11350			-0.35	28.38	3.0	4.3	1320	1
14:00	5888	29885	20	11370			-0.36	28.10	3.0	4.1	1319	1
15:00	7854	37739	12	11382			-0.35	28.23	3.0	4.2	1315	1
16:00	6539	44278	4388	15770			-0.36	28.10	4.3	4.0	1306	1
17:00	6408	50686	3588	19358			-0.34	28.23	3.0	4.9	1314	1
18:00	7851	58537	3433	22791			-0.35	28.33	3.0	3.6	1313	1
19:00	6733	65270	3251	26042			-0.35	28.23	3.0	3.7	1305	1
20:00	6255	71525	3700	29742			-0.35	28.23	3.0	4.5	1307	1
21:00	6251	77776	4515	34257			-0.35	28.25	3.0	3.7	1306	1
22:00	6180	83956	5420	39677			-0.35	28.25	3.0	4.8	1303	1
23:00	5947	89903	6318	45995			-0.35	28.23	3.0	3.6	1310	1
	3746	89903	1916	45995			-0.35	28.03	3.6	4.5	1305	24

*** N.I.B. == Incinerator was not in burn mode.***

PROCESS OXYGEN DAILY (MANUAL) CALIBRATION APROX TIME: 10:02 BY: KC

Calibration Results of THC and O2 Analyzers					Time of Calibration
	Bottle conc. (ppm)	Cylinder ID #	Zero (ppm)	Span (ppm)	8 : 15
THC	176	sx-34161	0.0	175.7	
O2	19.9	130	0.1	20.07	

Print Date: 8/24/99
Print Time: 10:50 AM

Date of Report
7/21/1999

Incinerator #6 "Daily" Report

Hour	Afterb. Temp. (F)	Breech Temp. (F)	Hrth. 1 Temp. (F)	Hrth. 2 Temp. (F)	Hrth. 3 Temp. (F)	Hrth. 4 Temp. (F)	Hrth. 5 Temp. (F)	Hrth. 6 Temp. (F)	Hrth. 7 Temp. (F)	Hrth. 8 Temp. (F)	Hrth. 9 Temp. (F)
0:00	914	952	1103	1118	1369	1448	1460	1503	1040	659	200
1:00	890	922	1068	1081	1322	1405	1465	1522	1040	688	201
2:00	899	938	1093	1105	1355	1432	1449	1500	1040	689	201
3:00	919	961	1116	1126	1373	1432	1455	1482	1040	666	200
4:00	897	929	1070	1081	1315	1386	1474	1513	1040	656	201
5:00	882	912	1055	1067	1298	1376	1459	1522	1040	667	199
6:00	886	920	1073	1084	1325	1391	1442	1506	1040	698	201
7:00	913	957	1113	1124	1367	1428	1459	1493	1040	669	199
8:00	896	929	1083	1099	1344	1430	1468	1504	1039	651	200
9:00	840	844	988	997	1206	1258	1458	1536	1041	675	201
10:00	797	792	944	952	1155	1220	1463	1547	1041	765	209
11:00	841	858	1017	1020	1159	1210	1469	1548	1050	781	219
12:00	897	935	1116	1122	1327	1405	1492	1521	1033	792	223
13:00	911	953	1122	1129	1407	1495	1451	1398	1006	704	204
14:00	948	999	1175	1185	1478	1554	1442	1405	1037	653	201
15:00	952	999	1167	1173	1486	1575	1447	1401	1055	683	202
16:00	976	1030	1196	1207	1496	1572	1439	1401	1052	686	202
17:00	950	983	1150	1158	1436	1502	1439	1417	1061	687	203
18:00	983	1037	1212	1220	1546	1637	1450	1388	1041	678	202
19:00	1005	1060	1246	1261	1591	1699	1438	1377	1033	673	201
20:00	970	1011	1192	1210	1535	1659	1415	1373	1031	669	199
21:00	962	1011	1189	1207	1516	1627	1416	1400	1044	673	201
22:00	959	999	1176	1195	1512	1627	1410	1375	1033	666	200
23:00	942	990	1165	1183	1479	1586	1412	1414	1050	667	201
	918	955	1118	1129	1392	1473	1449	1460	1040	687	203

Print Date: 8/24/99
Print Time: 10:50 AM

Mill Creek Waste Water Treatment Plant

Date of Report
7/21/1999

Incinerator #6 "Daily" Report

| | Scrubber | | | | | |
| Hour | RANGE LIMIT = | 26.0 | inches H2O | | | |
Minute=>	0	15	30	45	HrAvg	#<LIMIT
0:00	27.8	27.6	27.6	27.6	27.65	0
1:00	27.8	27.7	27.6	27.6	27.68	0
2:00	27.7	27.8	27.8	27.8	27.78	0
3:00	27.9	27.8	28.0	27.8	27.88	0
4:00	27.7	27.7	27.7	-- 27.7	27.70	0
5:00	27.8	27.6	27.8	27.7	27.73	0
6:00	27.6	27.8	27.9	28.1	27.85	0
7:00	28.0	27.9	27.8	27.8	27.88	0
8:00	27.8	27.7	27.8	28.0	27.83	0
9:00	28.1	28.0	27.7	27.6	27.85	0
10:00	27.7	27.6	27.8	28.4	27.88	0
11:00	28.1	28.4	28.3	28.4	28.30	0
12:00	28.1	28.3	28.2	28.2	28.20	0
13:00	28.3	28.3	28.5	28.4	28.38	0
14:00	28.2	28.1	28.0	28.1	28.10	0
15:00	28.3	28.2	28.2	28.2	28.23	0
16:00	28.2	28.1	28.0	28.1	28.10	0
17:00	28.3	28.3	28.2	28.1	28.23	0
18:00	28.2	28.3	28.5	28.3	28.33	0
19:00	28.2	28.2	28.2	28.3	28.23	0
20:00	28.3	28.3	28.1	28.2	28.23	0
21:00	28.3	28.3	28.2	28.2	28.25	0
22:00	28.3	28.3	28.2	28.2	28.25	0
23:00	28.2	28.2	28.3	28.2	28.23	0
					28.03	0

*** All values in brackets [ ] occured while incinerator was not in burn mode. ***

*** N.I.B. == Incinerator was not in burn mode. ***

Incinerator #6 "Daily" Report

					Flue Gas Opacity (%)							
Minute=> Hour	0	6	12	18	24	30	36	42	48	54	HrAvg	#>20	#>60
0:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
1:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
2:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
3:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
4:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
5:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
6:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
7:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
8:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
9:00	4	4	4	4	4	4	5	5	5	5	4.4	0	0
10:00	5	5	5	5	5	5	5	4	4	3	4.6	0	0
11:00	4	4	4	4	4	4	4	4	4	3	3.9	0	0
12:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
13:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
14:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
15:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
16:00	3	3	3	3	16	3	3	3	3	3	4.3	0	0
17:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
18:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
19:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
20:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
21:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
22:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
23:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
	3.5	3.5	3.5	3.5	4.1	3.5	3.6	3.5	3.5	3.5	3.6	0	0

OPACITY DAILY AUTOMATIC CALIBRATION AT TIME: 16:27

Metropolitan Sewer District of Greater Cincinnati and Hamilton County
Mill Creek Waste Water Treatment Plant

Date of Report
7/22/1999

Incinerator #6 "Daily" Report

Hour	Uncorr. THC (ppm)	CEM Oxygen (%)	Moist. H2O (%)	Corr. THC (ppm)	Rolling C. THC (ppm)	Sludge Feed (wet lb/hr)	Sludge Feed (dry lb/hr)	Accum. Sludge (dry tons)	LOWEST STATUS	HIGHEST STATUS	Report Event
0:00	21.0	12.86	3.18	37.70	38.64	14296	3095	1.55	BURN	BURN	NO
1:00	28.0	12.60	3.22	48.67	44.07	14156	3065	3.08	BURN	BURN	NO
2:00	21.0	10.87	3.16	34.39	40.25	14156	3065	4.61	BURN	BURN	NO
3:00	29.7	12.59	3.22	51.56	44.87	14156	3065	6.14	BURN	BURN	NO
4:00	20.6	12.67	3.12	35.81	40.59	14156	3065	7.68	BURN	BURN	NO
5:00	18.8	12.40	3.13	31.68	39.69	14156	3065	9.21	BURN	BURN	NO
6:00	21.6	13.65	3.13	42.45	36.65	14156	3065	10.74	BURN	BURN	NO
7:00	37.7	14.16	3.17	80.10	51.41	14156	3065	12.27	BURN	BURN	NO
8:00	32.5	12.66	3.20	57.30	59.95	14156	3065	13.81	BURN	BURN	NO
9:00	20.4	13.20	3.23	37.79	58.40	14156	3065	15.34	BURN	BURN	NO
10:00	20.1	12.59	3.23	34.61	43.23	14156	3065	16.87	BURN	BURN	NO
11:00	20.8	12.71	3.34	35.26	36.22	14156	3065	18.40	BURN	BURN	NO
12:00	18.5	12.47	3.34	31.41	34.09	14156	3065	19.94	BURN	BURN	NO
13:00	19.2	12.65	3.34	33.35	33.67	14156	3065	21.47	BURN	BURN	NO
14:00	18.2	12.35	3.34	30.59	31.78	14156	3065	23.00	BURN	BURN	NO
15:00	22.6	12.56	3.34	38.76	34.23	14156	3065	24.53	BURN	BURN	NO
16:00	24.7	11.90	3.34	39.42	36.26	14156	3065	26.07	BURN	BURN	NO
17:00	18.9	12.27	3.34	31.38	36.52	14156	3065	27.60	BURN	BURN	NO
18:00	23.7	9.83	3.35	33.05	34.62	14156	3065	29.13	BURN	BURN	NO
19:00	18.6	12.46	3.34	31.57	32.00	13993	3029	30.65	BURN	BURN	NO
20:00	23.4	12.42	3.32	39.57	34.73	14005	3032	32.16	BURN	BURN	NO
21:00	23.3	11.90	3.30	37.05	36.06	14223	3079	33.70	BURN	BURN	NO
22:00	22.9	12.60	3.30	39.25	38.62	14519	3143	35.27	BURN	BURN	NO
23:00	28.1	12.60	3.23	48.41	41.57	14595	3160	36.35	BURN	BURN	NO
	23.1	12.46	3.26	40.09	39.92	14185	3071	36.85			0

SludgeMultiplier = 0.216

*NOTE: FOR "YES" REPORT EVENT

O2 = HIGH OXYGEN VIOLATION   DP = LOW SCRUBBER DP VIOLATION
SQ = LOW SCRUBBER FLOW VIOLATION   OP = HIGH OPACITY VIOLATION

Date of Report
7/22/1999

Incinerator #6 "Daily" Report

Hour	Fuel N. Gas (scfh)	Accum. N. Gas (cf)	Fuel Digester (scfm)	Accum. Digester (cf)	Fuel Oil (gpm)	Accum. Fuel Oil (gal)	Furnace Pressure (in.H2O)	Scrubber D.P. (in.H2O)	Flue Opacity (%)	Breech O2 (%)	Scrub Q GPM	Inc. Burn Hours (hr)
0:00	6009	6009	7029	7029			-0.36	28.20	3.0	4.8	1303	1
1:00	5785	11794	7689	14718			-0.35	28.25	3.0	3.6	1313	1
2:00	6119	17913	8270	22988			-0.35	28.28	3.9	5.1	1313	1
3:00	5610	23523	7934	30922			-0.35	28.28	4.0	3.5	1308	1
4:00	6164	29687	4463	35385			-0.35	28.30	4.0	3.5	1309	1
5:00	4184	33871	1257	36642			-0.35	28.23	4.0	3.9 ·	1305	1
6:00	2983	36854	6	36648			-0.35	28.10	4.0	5.1	1312	1
7:00	1576	38430	6	36654			-0.35	28.00	4.0	5.6	1302	1
8:00	5028	43458	6	36660			-0.35	28.43	4.1	4.6	1297	1
9:00	6922	50380	105	36765			-0.35	28.50	4.0	5.0	1293	1
10:00	7768	58148	0	36765			-0.35	28.45	4.0	5.0	1296	1
11:00	7484	65632	6	36771			-0.35	28.45	4.0	5.0	1303	1
12:00	7326	72958	0	36771			-0.35	28.28	3.3	5.0	1299	1
13:00	7190	80148	0	36771			-0.35	28.28	3.0	5.2	1298	1
14:00	6035	86183	2755	39526			-0.35	28.03	3.0	5.8	1291	1
15:00	5871	92054	1874	41400			-0.35	27.83	3.0	5.5	1294	1
16:00	5567	97621	0	41400			-0.35	27.70	4.3	5.2	1288	1
17:00	7772	105393	6	41406			-0.35	27.78	3.0	4.9	1291	1
18:00	5221	110614	6	41412			-0.35	27.63	3.0	5.3	1287	1
19:00	7226	117840	6	41418			-0.36	27.75	3.0	5.6	1293	1
20:00	5775	123615	0	41418			-0.35	27.75	3.0	4.8	1285	1
21:00	6536	130151	0	41418			-0.36	27.90	3.0	5.4	1293	1
22:00	6496	136647	25	41443			-0.35	27.78	3.0	4.6	1292	1
23:00	3750	140397	31	41474			-0.35	27.83	3.0	6.4	1288	1
	5850	140397	1728	41474			-0.35	28.08	3.5	4.9	1298	24

*** N.I.B. == Incinerator was not in burn mode.***

PROCESS OXYGEN DAILY (MANUAL) CALIBRATION APROX TIME: 08:26   BY: KC

Calibration Results of THC and O2 Analyzers					Time of Calibration
	Bottle conc. (ppm)	Cylinder ID #	Zero (ppm)	Span (ppm)	8 : 15
THC	176	sx-34161	0.0	175.0	
O2	19.9	130	0.1	20.02	

Print Date: 8/24/99
Print Time: 10:46 AM

Metropolitan Sewer District of Greater Cincinnati and Hamilton County
Mill Creek Waste Water Treatment Plant

Date of Report
7/22/1999

Incinerator #6 "Daily" Report

Hour	Afterb. Temp. (F)	Breech Temp. (F)	Hrth. 1 Temp. (F)	Hrth. 2 Temp. (F)	Hrth. 3 Temp. (F)	Hrth. 4 Temp. (F)	Hrth. 5 Temp. (F)	Hrth. 6 Temp. (F)	Hrth. 7 Temp. (F)	Hrth. 8 Temp. (F)	Hrth. 9 Temp. (F)
0:00	944	985	1156	1174	1482	1590	1402	1382	1034	659	200
1:00	939	989	1166	1186	1473	1572	1419	1428	1053	665	200
2:00	931	966	1137	1155	1456	1566	1394	1380	1029	656	200
3:00	932	985	1157	1176	1460	1562	1418	1433	1054	663	200
4:00	964	1033	1197	1217	1528	1646	1403	1384	-- 1030	655	200
5:00	986	1057	1237	1257	1593	1724	1406	1375	1005	654	200
6:00	940	982	1156	1171	1524	1669	1401	1395	980	660	201
7:00	879	899	1063	1073	1289	1360	1432	1486	1028	699	208
8:00	946	989	1124	1131	1315	1390	1458	1506	1054	741	250
9:00	972	995	1100	1101	1398	1508	1418	1440	1004	678	250
10:00	989	1011	1122	1122	1437	1549	1424	1441	1010	676	251
11:00	990	1007	1117	1115	1434	1553	1431	1458	1016	682	250
12:00	1007	1028	1139	1136	1483	1613	1442	1462	1034	702	251
13:00	997	1007	1109	1105	1448	1565	1441	1467	1040	712	250
14:00	1002	1010	1113	1112	1466	1602	1447	1470	1057	733	250
15:00	966	965	1039	1038	1350	1454	1441	1493	1062	740	250
16:00	975	981	1080	1083	1372	1465	1441	1487	1056	732	250
17:00	980	994	1081	1084	1397	1500	1435	1445	1054	727	250
18:00	976	985	1082	1089	1355	1441	1449	1491	1056	716	250
19:00	972	980	1070	1073	1372	1474	1430	1449	1053	716	249
20:00	960	969	1049	1054	1312	1398	1440	1483	1057	715	251
21:00	970	978	1084	1089	1390	1496	1431	1461	1054	718	249
22:00	950	957	1034	1037	1305	1398	1437	1481	1057	732	251
23:00	922	906	980	983	1203	1271	1439	1532	1055	781	250
	962	986	1108	1115	1410	1515	1428	1451	1039	701	234

Date of Report
7/22/1999

Incinerator #6 "Daily" Report

			Scrubber			
	RANGE LIMIT =	26.0	inches H2O			
Minute=>	0	15	30	45	HrAvg	#<LIMIT
Hour						
0:00	28.2	28.1	28.2	28.3	28.20	0
1:00	28.3	28.3	28.2	28.2	28.25	0
2:00	28.2	28.4	28.3	28.2	28.28	0
3:00	28.3	28.2	28.2	28.4	28.28	0
4:00	28.3	28.4	28.2	28.3	28.30	0
5:00	28.3	28.4	28.1	28.1	28.23	0
6:00	28.1	28.1	28.1	28.1	28.10	0
7:00	27.9	27.8	28.1	28.2	28.00	0
8:00	28.5	28.5	28.3	28.4	28.43	0
9:00	28.4	28.5	28.6	28.5	28.50	0
10:00	28.5	28.4	28.4	28.5	28.45	0
11:00	28.4	28.4	28.5	28.5	28.45	0
12:00	28.5	28.3	28.1	28.2	28.28	0
13:00	28.3	28.3	28.3	28.2	28.28	0
14:00	28.1	28.1	28.0	27.9	28.03	0
15:00	27.9	27.9	27.8	27.7	27.83	0
16:00	27.5	27.8	27.7	27.8	27.70	0
17:00	27.7	27.6	27.8	28.0	27.78	0
18:00	27.6	27.5	27.7	27.7	27.63	0
19:00	27.8	27.8	27.7	27.7	27.75	0
20:00	27.8	27.7	27.8	27.7	27.75	0
21:00	27.8	27.8	27.9	28.1	27.90	0
22:00	28.0	27.7	27.8	27.6	27.78	0
23:00	27.9	27.7	27.7	28.0	27.83	0
					28.08	0

*** All values in brackets [ ] occured while incinerator was not in burn mode.***

*** N.I.B. == incinerator was not in burn mode.***

Print Date: 8/24/99
Print Time: 10:46 AM

Mill Creek Waste Water Treatment Plant

Incinerator #6 "Daily" Report

					Flue Gas Opacity (%)							
Minute=> Hour	0	6	12	18	24	30	36	42	48	54	HrAvg	#>20	#>60
0:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
1:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
2:00	3	4	4	4	4	4	4	4	4	4	3.9	0	0
3:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
4:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
5:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
6:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
7:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
8:00	4	5	4	4	4	4	4	4	4	4	4.1	0	0
9:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
10:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
11:00	4	4	4	4	4	4	4	4	4	4	4.0	0	0
12:00	4	4	4	3	3	3	3	3	3	3	3.3	0	0
13:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
14:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
15:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
16:00	3	3	3	3	16	3	3	3	3	3	4.3	0	0
17:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
18:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
19:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
20:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
21:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
22:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
23:00	3	3	3	3	3	3	3	3	3	3	3.0	0	0
	3.4	3.5	3.5	3.4	4.0	3.4	3.4	3.4	3.4	3.4	3.5	0	0

OPACITY DAILY AUTOMATIC CALIBRATION AT TIME: 16:27

APPENDIX N

Sampling and Analytical Protocols

N-1
PCB Protocols

N-1-1
Draft Air Emissions Method

Proposed Analytical Method for

Determination of Toxic Polychlorinated Biphenyl
Emissions from Sewage Incinerator Stationary Sources Using Isotope Dilution
High Resolution Gas Chromatography/High Resolution Mass Spectrometry

July 20, 1999

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Proposed Analytical Method for Determination of Toxic Polychlorinated Biphenyl Emissions from Sewage Incinerator Stationary Sources Using Isotope Dilution High Resolution Gas Chromatography/High Resolution Mass Spectrometry

1.0 SCOPE AND APPLICATION

1.1 This analytical method applies to the determination of toxic polychlorinated biphenyls (PCBs) in air emissions from sewage incinerator stationary sources at nanogram to picogram levels. The sensitivity which can ultimately be achieved for a given sample will depend upon the types and concentrations of other chemical compounds in the sample, as well as the original sample size and instrument sensitivity.

1.2 The analytical method presented here is intended to determine toxic PCBs in samples containing PCBs as single congeners or as complex mixtures. The target analytes are listed in Table 1.

1.3 The method is restricted for use only by or under the supervision of analysts experienced in the use of high resolution gas chromatography (HRGC)/high resolution mass spectrometry (HRMS), and skilled in the interpretation of mass spectra.

1.4 Because of the extreme toxicity of these compounds, the analyst must take necessary precautions to prevent exposure to himself/herself, or to others, of materials known or believed to contain PCBs.

2.0 SUMMARY OF METHOD

2.1 Particulate and gaseous phase PCBs are collected isokinetically from the stack and collected on a glass fiber filter, XAD-2 resin, and in impingers using a Modified Method 5 (MM5) sampling train. Procedures for MM5 sample collection are provided in EPA Method 0010. The MM5 samples consist of the filter, front and back half solvent rinses, the XAD-2 resin module, and impinger water and solvent rinses. The XAD-2 resin is pre-spiked with surrogate standards to monitor sampling efficiency during the sample collection. The preparation, pre-certification, and pre-spiking of the XAD-2 resin is described in Appendix A of this method. The preparation and pre-certification of the particulate filter is described in Appendix B of this method.

1

2.2   The field samples are combined into two separate fractions for extraction and analysis: (1) front half reagent rinses and filter; and (2) back half reagent rinses, XAD-2 resin, and the impinger water contents and reagent rinses.

2.3   The analytical flow diagram depicting the front and back half extraction procedures is shown in Figure 1. The samples are extracted using Soxhlet and/or solid phase extraction (SPE) techniques. Front and back half sample extracts are cleaned using acid/base partitioning, and silica and carbon column chromatography. The flow diagram depicting the cleanup procedures is shown in Figure 2. The separate front and back half extracts are analyzed using HRGC/HRMS.

   2.3.1   Isotopically labeled internal standards are added to each fraction separately before extraction.

   2.3.2   Isotopically labeled cleanup standards are added to the front half extract prior to sample cleanup. Isotopically labeled cleanup standards are not added to the back half extract (See Section 7.2.4.3).

   2.3.3   The PCB analytes in the processed extracts are separated with HRGC and identified and measured with HRMS. Results are quantified using relative response factors.

2.4   Various performance criteria are specified herein which the analytical data must satisfy to ensure the quality of the data. These represent minimum criteria which must be incorporated into any program in which toxic PCBs are determined in emissions from stationary sources.

3.0   DEFINITIONS AND ABBREVIATIONS

3.1   Definitions and Acronyms

   3.1.1   **Analyte** - a PCB compound measured by this method. The analytes are listed in Table 1.

   3.1.2   **Calibration Standard (CS)** - a solution prepared from a secondary standard and/or stock solutions and used to calibrate the response of the instrument with respect to analyte concentration.

   3.1.3   **Calibration Verification Standard (VER)** - the mid-point calibration standard (CS3) that is used to verify calibration. See Table 4.

   3.1.4   **Congener** - refers to a particular compound of the same chemical family.

2

3.1.5　CS1, CS2, CS3, CS4, CS5 - see calibration standards in Table 4.

3.1.6　HRGC - high resolution gas chromatograph or gas chromatography.

3.1.7　HRMS - high resolution mass spectrometer or mass spectrometry.

3.1.8　**Internal Standard (IS)** - a component which is added to every sample and is present in the same concentration in every blank, quality control sample, and calibration solution. The IS is added to the sample before extraction and is used to measure the concentration of the analyte and surrogate compound. The IS recovery serves as an indicator of the overall performance of the analysis.

3.1.9　**K-D** - Kuderna-Danish concentrator; a device used to concentrate the analytes in a solvent.

3.1.10　**Laboratory Blank** - see Laboratory Method Blank.

3.1.11　**Laboratory Method Blank** - an aliquot of reagent water or solvent that is treated exactly as a sample including exposure to all laboratory glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The laboratory method blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

3.1.12　**Laboratory Spike Sample** - a laboratory-prepared matrix blank spiked with known quantities of analytes. The laboratory spike sample is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in the method for precision and recovery.

3.1.13　**May** - this action, activity, or procedural step is neither required nor prohibited.

3.1.14　**May Not** - this action, activity, or procedural step is prohibited.

3.1.15　**Must** - this action, activity, or procedural step is required.

3.1.16　**m/z Scale** - the molecular mass to charge ratio scale.

3.1.17　**PAR** - precision and recovery standard; secondary standard used to prepare laboratory spike QC samples.

3.1.18　**Percent Relative Standard Deviation (%RSD)** - the standard deviation times 100 divided by the mean. Also termed "coefficient of variation."

3

3.1.19 **PFK** - perfluorokerosene; the mixture of compounds used to calibrate the exact m/z scale in the HRMS.

3.1.20 **Primary Dilution Standard** - a solution containing the specified analytes that is purchased or prepared from stock solutions and diluted as needed to prepare calibration solutions and other solutions.

3.1.21 **QC Check Sample** - a sample containing all or a subset of the analytes at known concentrations. The QC check sample is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

3.1.22 **Reagent Water** - water demonstrated to be free from the analytes of interest and potentially interfering substances at the analyte estimated detection limit; e.g., HPLC grade water.

3.1.23 **Recovery Standard** - a known amount of component added to the concentrated sample extract before injection. The response of the internal standards relative to the recovery standard is used to estimate the overall recovery of the internal standards.

3.1.24 **Relative Response Factor** - the response of the mass spectrometer to a known amount of an analyte relative to a known amount of an internal standard.

3.1.25 **RF** - response factor. See Section 10.2.2.

3.1.26 **RPD** - relative percent difference, defined as the absolute value of the difference between two values divided by the mean of the two values, expressed as a percentage.

3.1.27 **S/N** - signal to noise ratio.

3.1.28 **Should** - this action, activity, or procedural step is suggested but not required.

3.1.29 **SICP** - selected ion current profile; the line described by the signal at an exact m/z.

3.1.30 **SPE** - solid-phase extraction; an extraction technique in which an analyte is extracted from an aqueous sample by passage over or through a material capable of reversibly adsorbing the analyte. Also termed liquid-solid extraction.

4

3.1.31 Specific Isomers - a specific isomer is designated by indicating the exact positions (carbon atoms) where chlorines are located within the molecule. For example, 2,3,3',4,4'-PeCB refers to only one of the 209 possible PCB isomers - that isomer which is chlorinated in the 2,3,3',4,4'-position of the biphenyl ring structure.

3.1.32 Specificity - the ability to measure an analyte of interest in the presence of interferences and other analytes of interest encountered in a sample.

3.1.33 Stock Solution - a solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

3.1.34 Surrogate Standard - a labeled analyte is added in a known amount to the XAD-2 resin of the sampling train prior to sampling, and allowed to equilibrate with the matrix before the gaseous emissions are sampled. Its measured concentration in the extract is an indication of the sampling efficiency and possible sample breakthrough during the sample collection. The surrogate standard has to be a component that can be completely resolved, is not present in the sample, and does not have any interference effects.

3.1.35 Toxic PCB - any or all of the toxic chlorinated biphenyl isomers shown in Table 1.

3.1.36 VER - see Calibration Verification Standard (Section 3.1.3).

3.2   Abbreviations

3.2.1   **PCB** - any or all of the 209 possible polychlorinated biphenyl isomers.

3.2.2   **TCB** - abbreviation for tetrachlorinated biphenyl.

3.2.3   **PeCB** - abbreviation for pentachlorinated biphenyl.

3.2.4   **HxCB** - abbreviation for hexachlorinated biphenyl.

3.2.5   **HpCB** - abbreviation for heptachlorinated biphenyl.

3.2.6   **DCB** - abbreviation for decachlorinated biphenyl.

5

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated backgrounds at the ions monitored. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing field and laboratory blanks as described in Sections 9.1.1 and 9.2.2.

4.2 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, reagents are cleaned by extraction or solvent rinsing. The toxic PCB congeners 105, 114, 118, 123, 156, 157, 167, and 180 have been shown to be very difficult to completely eliminate from the laboratory, and baking of glassware in a kiln or furnace at 450-500°C may be necessary to remove these and other contaminants.

4.3 Proper cleaning of glassware is extremely important because glassware may not only contaminate the samples but may also remove the analytes of interest by adsorption onto the glass surface.

    4.3.1 Glassware should be rinsed with methanol and washed with a detergent solution as soon after use as is practical. Sonication of glassware containing a detergent solution for approximately 30 seconds may aid in cleaning. Glassware with removable parts, particularly separatory funnels with fluoropolymer stopcocks, must be disassembled prior to detergent washing.

    4.3.2 After detergent washing, glassware should be rinsed immediately; first with methanol, then with hot tap water. The tap water rinse is followed by distilled water, methanol, and then methylene chloride rinses.

    4.3.3 Baking of glassware in kiln or other high temperature furnace (450-500°C) may be warranted after particularly dirty samples are encountered. However, baking should be minimized, as repeated baking of glassware may cause active sites on the glass surface that may irreversibly adsorb PCBs.

    4.3.4 Immediately prior to use, the Soxhlet apparatus should be pre-extracted with methylene chloride for 3 hours to remove any possible background contamination.

4.4 The use of high purity reagents minimizes background contamination and interference problems. Purification of solvents by distillation in all-glass systems may be required.

4.5   Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences may vary considerably with the source being sampled. Toxic PCBs are often associated with other interfering chlorinated compounds which are at concentrations several orders of magnitude higher than that of the PCBs of interest. The cleanup procedures in Section 11.3 can be used to reduce many of these interferences, but unique samples may require additional cleanup approaches.

4.6   Two high resolution capillary columns, a J&W DBXLB, 60 m x 0.25 mm x 0.25 μm (J&W), and a 50 m x 0.23 mm x 0.25 μm HT-8 (SGE), are recommended for PCB analysis because both of these columns will resolve all 13 toxic PCBs. Equivalent columns that sufficiently resolve the toxic PCBs may also be used.

4.7   If other gas chromatographic conditions or other techniques are used, the analyst is required to support the data through an adequate quality assurance program.

5.0   SAFETY

5.1   The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Nevertheless, each chemical compound should be treated as a potential health hazard. Therefore, exposure to these chemicals must be reduced to the lowest possible level by whatever means available.

5.2   The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data (MSD) sheets should also be made available to all personnel involved in the chemical analysis.

5.3   PCBs and methylene chloride have been classified as known or suspected human or mammalian carcinogens.

6.0   EQUIPMENT AND SUPPLIES

6.1   Balances

        6.1.1   Analytical—Capable of weighing 0.1 mg.

        6.1.2   Top loading—Capable of weighing 10 mg.

6.2   Extraction Apparatus

        6.2.1   Solid Phase Extraction (SPE); for impinger water.

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SPE manifold, and a vacuum source capable of maintaining 25 in. Hg, equipped with shutoff valve and vacuum gauge shall be used. SPE columns containing octadecyl (C_{18}) bonded silica uniformly enmeshed in an inert matrix—Fisher Scientific 14-378°F (or equivalent) are used to extract the impinger water. Equivalent extracting procedures may be used to extract the target analytes from the impinger water.

6.2.2   Soxhlet Extraction; for XAD-2 resin and particulate filter.

The XAD-2 resin and particulate filters will be extracted using the Soxhlet technique. The Soxhlet extractor shall be a 50-mm ID, 200-mL capacity with 500-mL flask (Cal-Glass LG-6900, or equivalent, except substitute 500-mL round-bottom flask for 300-mL flat-bottom flask). The heating mantle shall be hemispherical to fit 500-mL round-bottom flask (Cal-Glass LG-8801-112, or equivalent). The heating mantle is controlled with a variable transformer(Powerstat, or equivalent), 110 volt, 10 amp.

6.3   Filtration Apparatus

6.3.1   Pyrex Glass Wool—heated in an oven at 450-500°C for 8 hours minimum.

6.3.2   Glass Funnel—125- to 250-mL.

6.3.3   Glass Fiber or Quartz Fiber Filter Paper—Whatman GF/D (or equivalent).

6.4   Cleanup Apparatus

6.4.1   Drying Column—15- to 20-mm ID Pyrex chromatographic column equipped with coarse-glass frit or glass-wool plug.

6.4.2   Pipets

6.4.2.1   Disposable, Pasteur, 150-mm long × 5-mm ID (Fisher Scientific 13-678-6A, or equivalent).

6.4.2.2   Disposable, serological, 25-mL (8- to 10- mm ID).

6.4.3   Glass Chromatographic Columns

6.4.3.1   150-mm long × 8-mm ID, (Kontes K-420155, or equivalent) with coarse-glass frit or glass-wool plug and 250-mL reservoir.

6.4.3.2   200-mm long × 15-mm ID, with coarse-glass frit or glass-wool plug and 250-mL reservoir.

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6.5.2.3　300-mm long × 22-mm ID, with coarse-glass frit, 300-mL reservoir, and glass or fluoropolymer stopcock.

6.5.3　HPLC/GPC

6.5.3.1　HPLC with a UV detector.

6.5.3.2　Autosampler capable of injecting 500 to 600 μL of sample.

6.5.3.3　Programmable fraction collector.

6.5.3.4　Recorder or integrator capable of recording the signal from a UV detector.

6.5.3.5　60 mL fraction collector vials/tubes.

6.5.3.6　Liquid chromatography pump capable of providing a constant flow of 5 or 10 mL/min.

6.5.3.7　122.5 x 300 mm, 100 Å pore size, Phenogel GPC/size exclusion column.

6.5.3.8　7.8 x 50 mm Phenogel precolumn.

6.5.4　Oven—For baking and storage of adsorbents, capable of maintaining a constant temperature (±5°C) in the range of 105-250°C.

6.6　Concentration Apparatus

6.6.1　Rotary evaporator—Buchi/Brinkman-American Scientific No. E5045-10 or equivalent, equipped with a variable temperature water bath.

6.6.1.1　Vacuum source for rotary evaporator equipped with shutoff valve at the evaporator and vacuum gauge.

6.6.1.2　A recirculating water pump and chiller are recommended, as use of tap water for cooling the evaporator wastes large volumes of water and can lead to inconsistent performance as water temperatures and pressures vary.

6.6.1.3　Round-bottom flask—100-mL and 500-mL or larger, with ground-glass fitting compatible with the rotary evaporator.

6.6.2　Kuderna-Danish (K-D) concentrator

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6.4.3.3　300-mm long x 22-mm ID, with coarse-glass frit, 300-mL reservoir, and glass or fluoropolymer stopcock.

6.4.3.4　Oven—For baking and storage of adsorbents, capable of maintaining a constant temperature (±5°C) in the range of 105-250°C.

6.5　Concentration Apparatus

6.5.1　Rotary Evaporator—Buchi/Brinkman-American Scientific No. E5045-10 or equivalent, equipped with a variable temperature water bath and vacuum source. A recirculating water pump and chiller are recommended, as use of tap water for cooling the evaporator wastes large volumes of water and can lead to inconsistent performance if water temperatures and pressures vary.

6.5.2　Kuderna-Danish (K-D) Concentrator—Concentrator tubes (10-mL graduated, Kontes K-570050-1025, or equivalent), ground-glass stoppers (size 19/22 joint) to prevent evaporation of extracts, evaporation flasks (500-mL, Kontes K-570001-0500, or equivalent), Snyder column (three-ball macro, Kontes K-503000-0232, or equivalent) may be used.

6.5.2.1　Glass or silicon carbide boiling chips-approximately 10/40 mesh, should be extracted with methylene chloride, and baked at 450°C for 1 hour minimum.

6.5.2.2　Fluoropolymer chips (optional) shall be extracted with methylene chloride prior to use. A heated water bath capable of maintaining a temperature within ±2°C shall be used in a fume hood.

6.5.3　Nitrogen Blowdown Apparatus—Equipped with water bath controlled in the range of 30 - 60°C (N-Evap, Organomation Associates, Inc., or equivalent), installed in a fume hood may be used.

6.5.4　TurboVap Nitrogen Blowdown—Turbovap II, Zymark, or equivalent may be used, equipped with concentrator tubes (Turbotubes, or equivalent).

6.6　Analytical Instrumentation

6.6.1　Gas Chromatograph—Shall have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and shall meet all of the performance specifications in Section 10.

6.6.2　GC Columns—Each of the GC columns listed below is capable of resolving the 13 toxic PCB congeners analyzed for in this method. Other

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GC columns may be used so long as resolution of the PCB congeners of concern from their most closely eluting leading and trailing congeners can be demonstrated.

6.6.2.1 Column #1—50 m long × 0.25±0.02-mm ID; 0.25-μm film HT-8 (SGE, or equivalent).

6.6.2.2 Column #2—60 m long x 0.25±0.02-mm ID; 0.25-μm film DBXLB (J&W, or equivalent).

6.6.3 Amber Glass Sample Vials—1 to 2-mL with fluoropolymer-lined screw-cap.

6.6.4 Amber Glass Vials—0.3-mL, conical, with fluoropolymer-lined screw or crimp cap.

6.6.5 High Resolution Mass Spectrometer—28- to 40-eV electron ionization, shall be capable of repetitively selectively monitoring 12 exact m/z's minimum at high resolution (≥10,000) during a period less than 1.5 seconds, and shall meet all of the performance specifications in Section 10.

6.6.6 HRGC/HRMS Interface—The high resolution mass spectrometer (HRMS) shall be interfaced to the high resolution gas chromatograph (HRGC) such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beams.

6.6.7 Data System—Capable of collecting, recording, and storing MS data.

7.0 REAGENTS AND STANDARDS

Note: unless otherwise stated, all reagents, water, and solvents must be pesticide grade or equivalent.

7.1 Sample Preparation and Analysis Reagents

7.1.1 pH Adjustment and Acid and Base Partitioning

7.1.1.1 Potassium Hydroxide—Dissolve 20 g of pesticide grade (if available) KOH in 100 mL reagent water.

7.1.1.2 Sulfuric Acid—Pesticide grade (if available; specific gravity 1.84).

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7.1.1.3   Hydrochloric Acid—Pesticide grade (if available), 6N.

7.1.1.4   Sodium Chloride—Pesticide grade (if available), prepare at 5 percent (w/v) solution in reagent water.

7.1.1.5   Desiccant—EM Science silica gel Grade H Type IV Indicating (6-16 mesh).

7.1.2   Solution Drying and Evaporation

7.1.2.1   Solution Drying—Sodium sulfate, pesticide grade (if available), granular, anhydrous (Baker 3375, or equivalent), rinsed with methylene chloride (20 mL/g), baked at 400°C for 1 hour minimum, cooled in a desiccator, and stored in a pre-cleaned glass bottle with screw-cap that prevents moisture from entering. If, after heating, the sodium sulfate develops a noticeable grayish cast (due to the presence of carbon in the crystal matrix), that batch of reagent is not suitable for use and should be discarded. Extraction with methylene chloride (as opposed to simple rinsing) and baking at a lower temperature may produce sodium sulfate that is suitable for use.

7.1.2.2   Prepurified Nitrogen—99.9995% purity.

7.1.3   Extraction

Solvents—Acetone, n-hexane, methanol, methylene chloride, and nonane; distilled in glass, pesticide quality, lot-certified to be free of interferences.

7.1.4   Extract Cleanup Adsorbents

7.1.4.1   Activated Silica Gel—100-200 mesh, Supelco 1-3651 (or equivalent), rinsed with methanol and methylene chloride, then extracted with methylene chloride for 3 hours, baked at 45°C for a half hour, then increased to 140-150°C for a minimum of 1 hour, cooled in a desiccator at room temperature, and stored in a precleaned glass bottle with screw-cap that prevents moisture from entering.

7.1.4.2   Acid Silica Gel (30 percent w/w)—Thoroughly mix 15 mL of concentrated sulfuric acid with 35 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a screw-capped bottle with fluoropolymer-lined cap.

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7.1.4.3 Basic Silica Gel—Thoroughly mix 17 mL of 1N sodium hydroxide with 35 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a screw-capped bottle with fluoropolymer-lined cap.

7.1.4.4 Carbopak C—(Supelco 1-0258, or equivalent), and Celite 545—(Supelco 2-0199, or equivalent). Thoroughly mix 18 g Carbopak C and 18 g Celite 545 to produce a 50 percent w/w mixture. Activate the mixture at 130°C for a minimum of 6 hours. Store in a desiccator.

7.2 Standard Solutions

Standards purchased as solutions or mixtures with certification to their purity, concentration, and authenticity, or prepared from materials of known purity and composition. If the chemical purity is 98 percent or greater, the weight may be used without correction to compute the concentration of the standard. Standards should be stored in the dark in a freezer at ≤0°C in screw-capped vials with fluoropolymer-lined caps when not being used. A mark is placed on the vial at the level of the solution so that solvent loss by evaporation can be detected. If solvent loss has occurred, or the shelf life has expired, the solution should be replaced.

7.2.1 Stock Standard Solutions

7.2.1.1 Prepared in nonane per the steps below or purchase as dilute solutions (Cambridge Isotope Laboratories (CIL, Woburn, MA, or equivalent). Observe the safety precautions in Section 5.

7.2.1.2 An appropriate amount of assayed reference material is dissolved in solvent. For example, weigh 1 to 2 mg of PCB 126 to three significant figures in a 10-mL ground-glass-stoppered volumetric flask and fill to the mark with nonane. After the PCB is completely dissolved, transfer the solution to a clean 15-mL vial with fluoropolymer-lined cap.

7.2.1.3 Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards. Reference standards that can be used to determine the accuracy of calibration standards are available from several vendors.

7.2.2 Precision and Recovery (PAR) Stock Solution

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Using the solutions in Section 7.2.1, prepare the PAR stock solution to contain the PCBs of interest at the concentrations shown in Table 3. When diluted, the solution will become the PAR spiking solution (Section 7.2.7).

7.2.3   Internal Standard Solutions

7.2.3.1   Internal Standard Stock Solution

From stock standard solutions, or from purchased mixtures, prepare this solution to contain the labeled internal standards in nonane at the stock solution concentrations shown in Table 3. This solution is diluted with methylene chloride prior to use (Section 7.2.3.2).

7.2.3.2   Internal Standard Spiking Solution

Dilute a sufficient volume of the labeled compound solution (Section 7.2.3.1) by a factor of 500 with acetone to prepare a diluted spiking solution. Concentrations may be adjusted to compensate for background levels. Each sample requires 1.0 mL of the diluted solution.

7.2.4   Surrogate Standard Spiking Solution

7.2.4.1   Prepare labeled PCBs 81 and 111 in acetone at the levels shown in Table 3.

7.2.4.2   The solution functions as a cleanup standard for the front half, and is added to the filter/front half extract prior to cleanup to measure the efficiency of the cleanup process.

7.2.4.3   Surrogate standards are not added to the XAD-2/back half extract prior to cleanup, since labeled PCB 81 and 111 are spiked onto the XAD-2 resin prior to shipment of the XAD-2 module into the field (Section 9.1.2).

7.2.4.4   The efficiency of the cleanup process for the XAD-2/back half extract can be measured by the recoveries of the internal standards.

7.2.5   Recovery Standard(s) Spiking Solution

Prepare the recovery standard spiking solution to contain labeled PCBs 52, 101, 138, and 178 in nonane at the level shown in Table 3.

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7.2.6 Calibration Standards (CS1 through CS5)

    7.2.6.1 Combine the solutions in Sections 7.2.1 to produce the five calibration solutions shown in Table 4 in nonane.

    7.2.6.2 Calibration standards may also be purchased already prepared in nonane (CIL).

    7.2.6.3 The prepared solutions permit the relative response (labeled to native) to be measured as a function of concentration. The CS3 standard is used for calibration verification (VER).

7.2.7 Precision and Recovery (PAR) Spiking Solution

    7.2.7.1 Used for preparation of laboratory spike QC samples (Section 9.2.4).

    7.2.7.2 Dilute 200 µL of the PAR stock solution (Section 7.2.2) to 10 mL with acetone. Each laboratory spike QC sample requires 1.0 mL.

7.2.8 GC Retention Time Window Defining and Isomer Specificity Test Solution

    7.2.8.1 This solution is used to define the beginning and ending retention times for the PCB congeners and to demonstrate isomer specificity of the GC columns.

    7.2.8.2 The solution must contain the compounds listed in Table 8 (CIL, or equivalent), at a minimum.

7.2.9 QC Check Sample

If available, a QC check sample should be obtained from a source independent of the calibration standards. Ideally, this check sample should be a certified standard reference material (SRM) containing the PCBs in known concentrations in a sample matrix similar to the matrix being analyzed.

7.2.10 Solution Stability

    7.2.10.1 Standard solutions used for quantitative purposes (Section 7.2.6) should be analyzed periodically, and should be assayed against reference standards before further use.

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7.2.10.2 If the analysis yields standard concentrations that are not within 25% of the true value for any PCB, the solutions will be replaced with solutions that, when analyzed, yield concentrations that are within 25% of the true value.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection

Emission samples to be analyzed for toxic PCBs by this method are collected according to EPA Modified Method 5 (MM5) procedures, or equivalent. Sample collection procedures are fully described in EPA Method 0010, and are not reproduced in this analytical method. The following sample fractions are generated using MM5 sampling procedures and provided to the laboratory for PCB determination:

Front Half Sample Fractions
- Particulate Filter (Container No. 1)
- Front Half Acetone/Methylene Chloride Reagent Rinses (Container No. 2)

Back Half Sample Fractions
- XAD-2 Module (Container No. 3)
- Back Half Acetone/Methylene Chloride Reagent Rinses (Container No. 4)
- Impingers Water Contents (Container No. 5)
- Impingers Acetone/Methylene Chloride Reagent Rinses (Container No. 6)

8.2 Storage

Solvent, filter, and XAD-2 sample fractions should be stored at the laboratory in the dark at $\leq 4°C$. Aqueous sample fractions should be stored at the laboratory in the dark at $4°C$ to prevent freezing.

8.3 Holding Times

All samples must be extracted within 30 days of collection and analyzed within 45 days of extraction.

9.0 QUALITY CONTROL

9.1 Sampling Quality Assurance/Quality Control

The positive identification and quantification of PCBs in stationary source emissions are highly dependent on the integrity of the samples received and the precision and accuracy of the analytical procedures employed. The QA

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procedures described in this section are to be used to monitor the performance of the sampling methods, identify problems, and effect solutions.

9.1.1 Field, Reagent, and Method Blanks

Field, reagent, and method blanks are collected to monitor the possibility of contamination from train components, field reagents, glassware, and shipment procedures.

9.1.2 XAD-2 Resin Pre-Spiked Surrogate Standards

Standards are pre-spiked onto each XAD-2 resin module prior to shipment to the field. The XAD-2 resin pre-spiking procedure is described in Appendix A of this method. The spiking compounds should be the stable, isotopically labeled analog of the compounds of interest, or a compound that will exhibit properties similar to the compounds of interest. Surrogate standards function to monitor sampling efficiency and possible compound breakthrough during sampling.

9.2 Analytical Method Quality Assurance/Quality Control

The minimum requirements of this method consist of spiking samples with labeled compounds to evaluate and document analyte recovery, and preparation and analysis of QC samples including blanks and duplicates. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance requirements of the method.

9.2.1 Labeled Compounds

The laboratory shall spike all samples with the labeled standard spiking solution (Sections 7.2.3.2 and 7.2.4) to assess method performance on the sample matrix. Recovery of labeled standards from samples should be assessed and records should be maintained.

9.2.1.1 Analyze each sample according to the procedures in Section 11. Compute the percent recovery of the labeled standards (Section 12.2.3).

9.2.1.2 The recovery of each labeled compound will be compared with the targeted limits in Table 5. If the recovery of any compound falls outside of these limits the data will be flagged and impact on reported concentration will be discussed in the reported results.

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9.2.2   Laboratory Method Blanks

   9.2.2.1   Prepare, extract, clean up, and concentrate a laboratory method
            blank with each sample batch (samples of the same matrix started
            through the extraction process on the same 12-hour shift, to a
            maximum of 20 samples). A laboratory method blank will
            consist of clean XAD-2 resin, two particulate filters, and all
            solvents/reagents in the approximate volumes normally received
            from the field.

   9.2.2.2   If any native PCB (Table 1) is found in the blank at greater than
            20 percent of the concentration level found in the sample, the
            reported data should be flagged as potentially containing some
            contribution from laboratory procedures.

9.2.3   QC Check Sample

   If available, analyze a QC check sample (Section 7.2.9) periodically to
   assure the accuracy of calibration standards and the overall reliability of
   the analytical process. It is suggested that the QC check sample be
   analyzed at least quarterly.

9.2.4   Laboratory Spike Samples

   9.2.4.1   With each sample batch, duplicate XAD traps not sent to the
            field are spiked with PAR spiking solution (Section 7.2.7) and
            processed through the same extraction, cleanup, and analysis
            procedures as the field samples.

   9.2.4.2   Calculate precision for the duplicate laboratory spike samples as
            the relative percent difference (RPD). The RPD should be ≤30
            percent.

   9.2.4.3   Calculate accuracy for the laboratory spike samples by
            determining the percent recovery of spiked analytes. Accuracy
            should be within 70-130 percent for analytes spiked 5 times the
            background level of the train blank.

   9.2.4.4   Any results outside of the above criteria will be flagged and the
            impact on reported concentrations discussed in the reported
            results.

9.2.5   The front half and back half fractions are processed and analyzed as
        separate extracts. This approach enhances QA/QC by enabling the analyst

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to pinpoint possible contamination and analyte losses to either the front or back half fractions of the sampling train.

9.2.6   The specifications contained in this method can be met if the apparatus used is calibrated properly and then maintained in a calibrated state.

9.2.6.1   The standards used for calibration (Section 10), calibration verification (Section 10.3.2), and for laboratory spike samples (Section 9.2.4) should be identical, so that the most precise results will be obtained.

9.2.6.2   A HRGC/HRMS instrument will provide the most reproducible results if dedicated to the settings and conditions required for the analyses of PCBs by this method.

10.0   HRGC/HRMS CALIBRATION

10.1   Operating Conditions

Establish the operating conditions necessary to meet the minimum retention times for the internal and recovery standards in Table 2.

10.1.1   Suggested HRGC Operating Conditions

Injector temperature: 290°C
Interface temperature: 290°C
Initial temperature: 150°C
Initial time: 2 min
Temperature program: 150 to 200°C at 10°C/min; 200 to 280°C at 2°C/min

NOTE: All portions of the column that connect the HRGC to the ion source shall remain at or above the interface temperature specified above during analysis to preclude condensation of less volatile compounds.

The HRGC conditions may be optimized for compound separation and sensitivity. Once optimized, the same HRGC conditions must be used for the analysis of all standards, blanks, and samples.

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10.1.2   High Resolution Mass Spectrometer (HRMS) Resolution

10.1.2.1   Obtain a selected ion current profile (SICP) of each analyte
listed in Table 3 at the two exact m/z's specified in Table 6 and
at ≥10,000 resolving power by injecting an authentic standard
of the PCBs either singly or as part of a mixture in which there
is no interference between closely eluted components.

10.1.2.2   The analysis time for PCBs may exceed the long-term mass
stability of the mass spectrometer. Because the instrument is
operated in the high-resolution mode, mass drifts of a few ppm
(e.g., 5 ppm in mass) can have serious adverse effects on
instrument performance. Therefore, a mass-drift correction is
mandatory and a lock-mass m/z from PFK is used for drift
correction. The lock-mass m/z is dependent on the exact m/z's
monitored within each descriptor, as shown in Table 6. The
level of PFK metered into the HRMS during analyses should
be adjusted so that the amplitude of the most intense selected
lock-mass m/z signal (regardless of the descriptor number)
does not exceed 10 percent of the full-scale deflection for a
given set of detector parameters. Under those conditions,
sensitivity changes that might occur during the analysis can be
more effectively monitored.

NOTE: Excessive PFK (or any other reference substance) may
cause noise problems and contamination of the ion source
necessitating increased frequency of source cleaning.

10.1.2.3   If the HRMS has the capability to monitor resolution during the
analysis, it is acceptable to terminate the analysis when the
resolution falls below 10,000 to save reanalysis time.

10.1.2.4   Using a PFK molecular leak, tune the instrument to meet the
minimum required resolving power of 10,000 (10 percent
valley) at m/z 380.9760. For each descriptor (Table 6),
monitor and record the resolution and exact m/z's of three to
five reference peaks covering the mass range of the descriptor.
The resolution must be greater than or equal to 10,000, and the
deviation between the exact m/z and the theoretical m/z
(Table 6) for each exact m/z monitored must be less than
5 ppm.

10.1.3   Ion Abundance Ratios, Minimum Levels, Signal-to-Noise Ratios, and
Absolute Retention Times

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10.1.3.1　Choose an injection volume of either 1- or 2-μL, consistent with the capability of the HRGC/HRMS instrument. Inject a 1- or 2-μL aliquot of the CS1 calibration solution (Table 4) using the GC conditions from Section 10.1.1.

10.1.3.2　Measure the SICP areas for each analyte, and compute the ion abundance ratios at the exact m/z's specified in Table 6. Compare the computed ratio to the theoretical ratio given in Table 7.

The exact m/z's to be monitored in each descriptor are shown in Table 6. Each group or descriptor shall be monitored in succession as a function of GC retention time to ensure that all of the toxic PCBs are detected. Additional m/z's may be monitored in each descriptor, and the m/z's may be divided among more than the descriptors listed in Table 6, provided that the laboratory is able to monitor the m/z's of all the PCBs that may elute from the GC in a given retention-time window.

The mass spectrometer shall be operated in a mass-drift correction mode, using PFK to provide lock m/z's. The lock mass for each group of m/z's is shown in Table 6. Each lock mass shall be monitored and shall not vary by more than ±20 percent throughout its respective retention time window. Variations of the lock mass by more than 20 percent indicate the presence of coeluting interferences that may significantly reduce the sensitivity of the mass spectrometer. Reinjection of another aliquot of the sample extract will not resolve the problem. Additional cleanup of the extract may be required to remove the interferences.

10.1.3.3　All PCBs and labeled compounds in the CS1 standard shall be within the QC limits in Table 7 for their respective ion abundance ratios; otherwise, the mass spectrometer shall be adjusted and this test repeated until the m/z ratios fall within the limits specified. If the adjustment alters the resolution of the mass spectrometer, resolution shall be verified (Section 10.1.2) prior to repeat of the test.

10.1.3.4　The peaks representing the PCBs and labeled compounds in the CS1 calibration standard must have signal-to-noise ratios (S/N) greater than or equal to 10.0. Otherwise, the mass spectrometer shall be adjusted and this test repeated until the peaks have S/N greater than or equal to 10.0.

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10.1.3.5 Retention Time Windows—Analyze the window defining
mixture (Section 7.2.8) using the optimized temperature
program in Section 10.1.1. Table 2 gives the elution order
(first/last) of the window-defining compounds.

10.1.4 Isomer Specificity

10.1.4.1 Analyze the isomer specificity test standard (Section 7.2.8)
using the procedure in Section 11.11 and the optimized
conditions for sample analysis (Section 10.1.1).

10.1.4.2 Compute the percent valley between the GC peaks for PCB
123 and PCB 118, and between the GC peaks for PCB 156 and
157.

10.1.4.3 Verify that the height of the valley between these closely eluted
isomers is less than 25 percent. If the valley exceeds 25
percent, adjust the analytical conditions and repeat the test or
replace the GC column and recalibrate.

10.2 Initial Calibration

10.2.1 Prepare a calibration curve encompassing the concentration range for
each compound to be determined. Referring to Table 2, calculate the
relative response factors for unlabeled target analytes (RF_n) relative to
their appropriate internal standard (Table 5) and the relative response
factors for the $^{13}C_{12}$-labeled internal standards (RF_{is}) using the four
recovery standards (Table 5) according to the following formulae:

$$RF_n = \frac{(A_n^1 + A_n^2) \times Q_{is}}{(A_{is}^1 + A_{is}^2) \times Q_n}$$

$$RF_{is} = \frac{(A_{is}^1 + A_{is}^2) \times Q_{rs}}{(A_{rs}^1 + A_{rs}^2) \times Q_{is}}$$

where:

A_n^1 *and* A_n^2 = *sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and
6) for unlabeled PCBs,*

A_{is}^1 *and* A_{is}^2 = *sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and
6) for the labeled internal standards,*

A_{rs}^1 *and* A_{rs}^2 = *sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and
6) for the recovery standard,*

Q_{is} = *quantity of the internal standard injected (pg),*

Q_{rs} = *quantity of the recovery standard injected (pg), and*

Q_n = *quantity of the unlabeled PCB analyte injected (pg).*

RF_n *and the* RF_{is} *are dimensionless quantities; the units used to express* Q_{is}, Q_{rs} *and* Q_n
must be the same.

10.2.2 Calculate the mean relative response factors and their respective percent relative standard deviation (%RSD) for the five calibration solutions. If the mean relative response factors between the analytes is not within 25% RSD, the instrument must be re-calibrated.

$$\overline{RF_n} = \frac{\sum_{j=1}^{5} RF_{n(j)}}{5}$$

where n represents a particular PCB congener (n = 1 to 13; Table 3), and j is the injection or calibration solution number; (j = 1 to 5).

$$\overline{RF_{is}} = \frac{\sum_{j=1}^{5} RF_{is(j)}}{5}$$

where is represents a particular PCB internal standard (is = 14 to 23; Table 3), and j is the injection or calibration solution number; (j = 1 to 5).

10.3 Operation Verification

At the beginning of each 12-hour shift during which analyses are performed, HRGC/HRMS system performance and calibration are verified for all native PCBs and labeled compounds. For these tests, analysis of the CS3 calibration verification (VER) standard (Section 7.2.6 and Table 4) and the isomer specificity test solution (Section 7.2.8 and Table 8) shall be used to verify all performance criteria. Adjustment and/or recalibration (Section 10) shall be performed until all performance criteria are met. Only after all performance criteria are met may samples and blanks be analyzed.

10.3.1 HRMS Resolution

A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at the appropriate m/z before any analysis is performed. Static resolving power checks must be performed at the beginning and at the end of each analysis batch according to procedures in Section 10.1.2. Corrective actions must be implemented whenever the resolving power does not meet the requirement.

10.3.2 Calibration Verification

10.3.2.1 Inject the VER standard using the procedure in Section 11.11.

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10.3.2.2 The m/z abundance ratios for all PCBs shall be within the limits in Table 7; otherwise, the mass spectrometer shall be adjusted until the m/z abundance ratios fall within the limits specified, and the verification test shall be repeated. If the adjustment alters the resolution of the mass spectrometer, resolution shall be verified (Section 10.1.2) prior to repeat of the verification test.

10.3.2.3 The peaks representing each native PCB and labeled compound in the VER standard must be present with a S/N of at least 10; otherwise, the mass spectrometer shall be adjusted and the verification test repeated.

10.3.2.4 Calculate the relative response factors (RF) for unlabeled target analytes [$RF_{(n)}$; n = 1 to 13 from Table 3] relative to their appropriate internal standards (Table 2), and the RF_{is} for the $^{13}C_{12}$-labeled internal standards [$RF_{(is)}$; is = 14-23] relative to the recovery standards (Table 2) using the equations shown in Section 10.2.1.

10.3.2.5 For each compound, compare the relative response factor with those generated in the initial calibration. Relative response factors should be within 35 percent of initial calibration results for 70% of the analytes for the calibration to be verified. Once verified, analysis of standards and sample extracts may proceed. If, however, fewer than 70% of the response factors are within the 35% limit, the measurement system is not performing properly for those compounds. In this event, prepare a fresh calibration standard or correct the problem causing the failure and repeat the resolution (Section 10.3.1) and calibration verification (Section 10.3.2) tests, or recalibrate (Section 10). Per the analyst's discretion, results may also be reported for these analytes using the average calibration verification response factors bracketing the samples rather than the mean response factor generated in the initial calibration. If this option is chosen, data reported using an average calibration verification response factor should be flagged and discussed in the final report.

10.3.3 Retention Times

The absolute retention times of the GC/MS internal standards in the calibration verification shall be within ±15 seconds of the retention times obtained during initial calibration.

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10.3.4 HRGC Resolution

    10.3.4.1 Inject the GC retention time window defining and isomer specificity test solution (Section 7.2.8).

    10.3.4.2 The valley height between PCBs 123 and 118 at m/z 325.8804 shall not exceed 25 percent, and the valley height between PCBs 156 and 157 shall not exceed 25 percent at m/z 359.8415 on the GC columns.

    10.3.4.3 If the absolute retention time of any compound is not within the limits specified or if the congeners are not resolved, the GC is not performing properly. In this event, adjust the GC and repeat the calibration verification test or recalibrate, or replace the GC column and either verify calibration or recalibrate.

10.4 Data Storage

MS data shall be collected, recorded, and stored.

10.4.1 Data Acquisition

The signal at each exact m/z shall be collected repetitively throughout the monitoring period and stored on a mass storage device.

10.4.2 Response Factors and Multipoint Calibrations

The data system shall be used to record and maintain lists of response factors and multipoint calibration curves. Computations of relative standard deviation (coefficient of variation) shall be used to test calibration linearity.

11.0 PROCEDURE

The analyst will receive the following six analytical fractions for each sample collected in the field:

Front Half Sample Fractions
- Particulate Filter (Container No. 1)
- Front Half Acetone/Methylene Chloride Reagent Rinses (Container No. 2)

Back Half Sample Fractions
- XAD-2 Module (Container No. 3)

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- Back Half Acetone/Methylene Chloride Reagent Rinses (Container No. 4)
- Impingers Water Contents (Container No. 5)
- Impingers Acetone/Methylene Chloride Reagent Rinses (Container No. 6)

The fractions corresponding to the front half of the sampling train, which are the particulate filter (Container No. 1) and the front half rinses (Container No. 2), will be extracted, combined, and cleaned for analysis using HRGC/HRMS.

The fractions corresponding to the back half of the sampling train, which are the XAD-2 resin module (Container No. 3), back half rinses (Container No. 4), and the impingers water and rinses (Containers Nos. 5 and 6, respectively) will be extracted, combined, and cleaned for a separate analysis using HRGC/HRMS.

11.1   Front Half Sample Extraction

The front half consists of the particulate filter and the front half rinses. The front half rinses are filtered to remove any particulate; the filter is combined with the particulate filter (Container No. 1), and both extracted together using the Soxhlet technique.

11.1.1   Front Half Acetone/Methylene Chloride Rinses (Container No. 2)

11.1.1.1   The front half rinse (Container No. 2) may contain particulate material which has been removed from the probe. To separate particulate matter from the front half rinse, filter the front half rinse. To avoid introducing any contamination, use the same type of filter which has been used in the sampling train, from the same lot as the filter in the train. Pour the front half rinse through the filter then rinse Container No. 2 three times with 10-mL aliquots of methylene chloride, and filter the methylene chloride rinses.

11.1.1.2   With the filtrate, proceed to Section 11.2 for water removal.

11.1.1.3   With the filter, proceed to Section 11.1.2.2 for Soxhlet extraction.

11.1.2   Particulate Matter Filter (Container No. 1)

11.1.2.1   Using clean forceps, place 10 boiling chips into the bottom of the round bottom flask of the Soxhlet extractor and connect the Soxhlet extractor to the round bottom flask.

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11.1.2.2 Using clean forceps, place the filter containing the particulate from Section 11.1.1.3 into a glass thimble, or place the filter on a plug of pre-clean glass wool.

11.1.2.3 Using clean forceps, place the particulate matter filter (Container No. 1) into the glass thimble or on the plug of pre-cleaned glass wool from Section 11.1.2.2.

11.1.2.4 Using a clean syringe or volumetric pipet, add a 1-mL aliquot of the internal standard spiking solution to the filter. If a laboratory spike sample is being prepared (Section 9.2.4), the PAR spiking solution will be added at this time. Add 1 mL of spiking solution uniformly onto the particulate-coated surface of the filter in the extractor by spotting small volumes at multiple filter locations, using a syringe. Repeat the spiking process with matrix spike solution, if these solutions are being used. Place a piece of pre-cleaned glass wool on top of the spiked filter in the extractor to keep the filters in place. Rinse the filter container three times with methylene chloride and add the rinses to the Soxhlet extractor.

11.1.2.5 Slowly add methylene chloride to the Soxhlet extractor containing the two filters through the Soxhlet (with condenser removed), allowing the Soxhlet to cycle. Add sufficient solvent to fill the round bottom flask approximately more than half full and submerge the filters.

11.1.2.6 Place a heating mantle under the round bottom flask and connect the upper joint of the Soxhlet to a condenser, making sure that the coolant is flowing through the condenser.

11.1.2.7 Allow the sample to extract for, at least, 12 hours but not more than 24 hours, adjusting the mantle temperature for cycling (flushing solvent from the Soxhlet into the round bottom flask) approximately once every 30 minutes.

11.1.2.8 After cooling, disconnect the extractor from the condenser. Tilt the Soxhlet slightly until the remaining solvent has drained into the round bottom flask.

11.1.2.9 Transfer the extract from the round bottom flask into a clean 500-mL amber glass bottle with PTFE-lined screw cap. Rinse the round bottom flask three times with approximately 10-mL aliquots of methylene chloride and transfer the rinses to the

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amber bottle. Store the filter extract at ≤0°C until the preparation of the filtered front half rinse has been completed.

11.1.2.10 Archive the extracted filters at ≤4°C until the GC/HRMS analysis is completed.

11.2 Front Half Sample Water Removal

Water is removed from the front half rinses and the particulate filter extract using sodium sulfate. During the drying procedure, the extracts are combined into a Kuderna-Danish setup.

11.2.1 Front Half Acetone/Methylene Chloride Rinses Filtrate (See Section 11.1.1.2)

11.2.1.1 Because the front half rinse sample consists of a mixture of acetone and methylene chloride and the rinse may also contain water, the water needs to be removed from the organic solvent before combining with the filter extract. Add 20 g of sodium sulfate (Na_2SO_4) to the rinse and allow to set for 10 minutes.

11.2.1.2 Using a clean pair of forceps, place a small portion of precleaned glass wool in the bottom of a glass funnel and pour a 2.45-m (1-in.) layer of Na_2SO_4 on top of the glass wool.

11.2.1.3 Rinse the Na_2SO_4 contained in the funnel three times with methylene chloride; discard the rinses. Support the funnel in a ring of clamp above the receiving container to prevent tipping.

11.2.1.4 Place the funnel into a clean KD concentrator, consisting of a 20 mL concentrator tube connected to a 500 mL evaporative flask. Slowly pour the extract from the dried front half rinse through the Na_2SO_4. Rinse the container containing the extract/Na_2SO_4 three times, using approximately 10 mL of methylene chloride each time. Add rinses to the funnel. Rinse the Na_2SO_4 with approximately 5 mL of methylene chloride to complete the transfer.

NOTE: During this process, monitor the condition of Na_2SO_4 to determine that the bed of Na_2SO_4 is not solidifying and exceeding its drying capacity. If the Na_2SO_4 bed can be stirred and is still free-flowing, effective moisture removal from the extracts is occurring. If the Na_2SO_4 bed is solidified, repeat Steps 11.2.1.1 to 11.2.1.3 to make a new drying funnel, and continue drying the extracts.

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11.2.1.5 If the volume of the extract is greater than 500 mL, collect the remaining dried sample extract into a clean amber bottle for subsequent concentration using the same K-D setup.

11.2.1.6 Reduce the volume of the extract to <10 mL following the procedures described in Section 11.3.

11.2.2 Particulate Filter Extract (See Section 11.1.2.9)

11.2.2.1 Prepare a Na_2SO_4 drying funnel, as described in Sections 11.2.1.2 and 11.2.1.3.

11.2.2.2 Place the funnel exit into the same 500 mL evaporative flask described in Section 11.2.1.4. Slowly pour the extract from the dried front half rinse through the Na_2SO_4. Rinse the container containing the extract/Na_2SO_4 three times, using approximately 10 mL of methylene chloride each time. Add rinses to the funnel. Rinse the Na_2SO_4 with approximately 5 mL of methylene chloride to complete the transfer.

Note: Monitor the condition of the Na_2SO_4 as noted in Section 11.2.1.4.

11.2.2.3 If the volume of the extract is greater than 500 mL, follow the procedures in Sections 11.2.1.5 and 11.2.1.6.

11.2.2.4 Proceed to Section 11.3.

11.3 Front Half Combined Filter Extract and Front Half Rinse Sample Reduction

The combined particulate filter extract and front half rinse sample is reduced in volume using a macro and micro Kuderna-Danish (K-D) apparatus, and half of the total extract is archived. The other half of the total extract is cleaned according to the procedures described in Section 11.4.

11.3.1 Using a clean pair of forceps, place five boiling chips into the concentrator tube. Attach a three-ball macro Snyder column to the K-D concentrator with clips or springs. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Attach the solvent vapor recovery glassware (condenser and collection device) to the Snyder column of the K-D apparatus. Place the K-D apparatus on a hot water bath (70-75°C) to remove methylene chloride; then to 80-85°C to remove acetone. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 20 to 30 minutes. Rinse sides of the K-D apparatus during concentration with a

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small volume of methylene chloride. When the apparent volume of the liquid reaches 6-8 mL, remove the K-D apparatus from the water bath and allow the apparatus to cool and drain for at least 5 minutes If the volume of extract to be concentrated is greater than 500 mL, repeat the concentration as many times as required using the same 500-mL evaporative flask and systematically add remaining extract (allow to cool slightly before addition of more extract). If repeated concentrations are performed, add two new boiling chips each time.

NOTE: Never let the extract in the concentrator tube go to dryness even though additional solvent is present in the upper portion of the K-D apparatus.

11.3.2 Remove the Snyder column and evaporative flask. With a clean pair of forceps, add two new boiling chips to the concentrator tube. Attach a micro Snyder column to the concentrator tube. Attach the solvent vapor recovery glassware (condenser and collection device) to the Snyder column of the K-D apparatus. Prewet the Snyder column with about 0.5 mL of methylene chloride. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in the hot water, while supporting the tube with a clamp or by gloved hands. When the apparent volume of the liquid reaches 4-5 mL, remove the K-D apparatus from the water bath and allow the apparatus to cool and drain for at least 5 minutes. If the volume is greater than 10 mL, add a new boiling chip to the concentrator tube, prewet the Snyder column, and concentrate again on the hot water bath. Remove any moisture from the outside of the concentrator tube.

11.3.3 Transfer the extract to a calibrated vial or a volumetric flask, rinse concentrator tube with a minimum volume of methylene chloride and add rinses to the vial, and add methylene chloride, if necessary, to attain a final volume of 10 mL.

11.3.4 Transfer 5.0 mL of the extract to a 10-mL glass storage vial with a PTFE-lined screw cap. Label the extract as "Archived Extract of Front Half" store at <0°C. Mark the liquid level on the vial with a permanent marker to monitor solvent evaporation during storage.

11.3.5 Place the remaining 5.0 mL of the extract through the sample cleanup procedure described in Section 11.4.

11 4   Front Half Combined Extract Cleanup

The un-archived portion of the front half extract is cleaned using acid and base partitioning, and silica gel and carbon column chromatography.

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11.4.1 Acid and Base Partitioning

11.4.1.1 Prior to acid and base partitioning, concentrate the extract to 1 mL using K-D evaporation, then add 5 mL of hexane and concentrate to 2 mL using K-D evaporation. Dilute the extract with 50 mL of hexane and transfer to a clean separatory funnel. Spike a known amount (1 mL) of the surrogate standard spiking solution (Section 7.2.4) into the filter/front half extract.

11.4.1.2 Partition the extract against 50 mL of sulfuric acid (Section 7.1.1). Shake for two minutes with periodic venting into a hood. Remove and discard the aqueous layer. Repeat the acid washing until no color is visible in the aqueous layer; using up to a maximum of four washings.

11.4.1.3 Partition the extract against 50 mL of 5 percent NaCl solution (Section 7.1.1) in the same way as with the acid. Discard the aqueous layer.

11.4.1.4 Partition the extract against 50 mL of potassium hydroxide solution (Section 7.1.1) in the same way as with the acid. Repeat the base washing until no color is visible in the aqueous layer; using up to a maximum of four washings. Minimize contact time between the extract and the base to prevent degradation of the PCBs.

11.4.1.5 Repeat the partitioning against the NaCl solution two more times, each time discarding the aqueous layer.

11.4.1.6 Pour the extract through a drying column containing 7 to 10 cm of granular anhydrous sodium sulfate (Section 7.1.2.1). Rinse the separatory funnel with 30 to 50 mL of hexane, and pour through the drying column. Collect the extract in a round-bottom flask. Concentrate the hexane extract to a volume of 4 mL for silica gel cleanup using either rotary evaporation, Kuderna-Danish apparatus, or Turbovap apparatus (Sections 11.4.1.6.1 and 11.4.1.6.3), then proceed to Section 11.4.2.

11.4.1.6.1 Rotary Evaporation

Note: Improper use of the rotary evaporator may result in contamination of the sample extract(s).

Concentrate the extract in a round-bottom flask. Assemble the rotary evaporator according to

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manufacturer's instructions, and warm the water bath to 45°C. On a daily basis, preclean the rotary evaporator by concentrating 100 mL of clean extraction solvent through the system. Archive both the concentrated solvent and the solvent in the catch flask for a contamination check if necessary. Between samples, use three 2- to 3-mL aliquots of solvent to rinse the feed tube between samples. Collect rinse in a waste beaker.

Attach the round-bottom flask containing the sample extract to the rotary evaporator. Slowly apply vacuum to the system, and begin rotating the sample flask. Lower the flask into the water bath, and adjust the speed of rotation and the temperature as required to complete concentration in 15 to 20 minutes. At the proper rate of concentration, the flow of solvent into the receiving flask must be steady, with no bumping or visible boiling of the extract occurring.

NOTE: If the rate of concentration is too fast, analyte loss may occur.

When the liquid in the concentration flask has reached an apparent volume of approximately 2 mL, remove the flask from the water bath and stop the rotation. Slowly and carefully admit air into the system. Be sure not to open the valve so quickly that the sample is blown out of the flask. Rinse the feed tube with approximately 2 mL of solvent.

11.4.1.6.2 Kuderna-Danish (K-D) Evaporation—Described in Sections 11.3.1 - 11.3.2.

11.4.1.6.3 Turbovap Evaporation—Concentrate the extracts in separate 250-mL Turbotubes. The Turbovap technique is used for solvents such as methylene chloride and n-hexane.

11.4.2 Silica Gel Cleanup

11.4.2.1 Place a glass-wool plug in a 15-mm ID chromatography column (Section 6.4.3.2). Pack the column bottom to top with

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1 g silica gel (Section 7.1.4.1), 4 g basic silica gel (Section 7.1.4.3), 1 g silica gel, 8 g acid silica gel (Section 7.1.4.2), 2 g silica gel, and 4 g granular anhydrous sodium sulfate (Section 7.1.2.1). Tap the column to settle the adsorbents.

11.4.2.2 Pre-elute the column with 20 to 30 mL of n-hexane. Discard the eluate. Check the column for channeling. If channeling is present, discard the column and prepare another.

11.4.2.3 Apply the concentrated extract (4 mL) to the column. Open the stopcock until the extract is within 1 mm of the sodium sulfate. Rinse the receiver three times with 4-mL portions of n-hexane, and apply separately to the column. Elute the PCB isomers with 75 mL of n-hexane and collect the eluate.

11.4.2.4 Concentrate the eluate to 1 mL per Section 11.3.2, then proceed to carbon column cleanup (Section 11.4.3).

11.4.3 Carbon Column

11.4.3.1 Cut both ends from a 25-mL disposable serological pipet (Section 6.4.2.2) to produce a 20-cm column. Fire-polish both ends and flare both ends if desired. Insert a glass-wool plug at one end, and pack the column with 3.6 g of Carbopak/Celite (Section 7.1.4.4) to form an adsorbent bed. Insert a glass-wool plug on top of the bed to hold the adsorbent in place.

11.4.3.2 Pre-elute the column with 20 mL each in succession of toluene, methylene chloride and n-hexane. When the solvent is within 1 mm of the column packing, apply the n-hexane sample extract to the column. Rinse the sample container twice with 1-mL portions of n-hexane and apply separately to the column. Apply 2 mL of n-hexane to complete the transfer.

11.4.3.3 Elute the column with 25 mL of n-hexane and collect the eluate. This fraction will contain the mono- and di-ortho PCBs.

11.4.3.4 Elute the column with 15 mL of methanol; collect and archive this fraction. This fraction contains potential interferents. If the recovery of labeled compounds is very low, this fraction can be analyzed in order to potentially ascertain where losses occurred.

11.4.3.5 Elute the column with 15 mL of toluene; collect the eluate.

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11.4.3.6 Filter the combined hexane and toluene fractions if evidence of carbon particles from the chromatography column is seen.

11.4.3.7 Concentrate the hexane and toluene fractions to a final volume of 1 mL using rotary, KD, and/or Turbovap (Section 11.4.1.6) evaporation techniques.

11.5 Front Half Combined Sample Concentration to Final Volume

The extract is concentrated to final volume, and the recovery standards are added.

11.5.1 The extract is concentrated in a calibrated microtube to a final volume of 20 μL to 1 mL, per the analyst's discretion, under a gentle stream of nitrogen.

11.5.2 Add 10 μL of the appropriate recovery standard solution (Section 7.2.5) to the sample extract.

11.5.3 Proceed to Section 11.11 for HRGC/HRMS analysis.

11.6 Back Half Sample Extraction

The back half consists of the XAD-2 module, the back half and impinger acetone/methylene chloride rinses, and the impinger water. The XAD-2 module is extracted using the Soxhlet technique, and the impinger water may be extracted using the solid phase extraction (SPE) technique. The back half and impinger acetone/methylene chloride rinses are not extracted, but combined during the drying process in Section 11.7.

11.6.1 XAD-2 Module (Container No. 3)

11.6.1.1 Using clean forceps, place 10 boiling chips in the bottom of the round flask of the Soxhlet extractor and connect the Soxhlet extractor to the round bottom flask.

11.6.1.2 Place a piece of pre-cleaned glass wool in the bottom and the side-arm of the Soxhlet extractor. Transfer the XAD-2 resin directly to the Soxhlet extractor and place on the top of the glass wool. To remove the XAD-2 resin from the sampling module, remove the glass wool from the end of the XAD-2 sampling module, and place this glass wool in the extractor. If the XAD-2 resin is wet and difficult to transfer, follow the procedure described in Section 7.4.2.2 of Method 3542. Rinse the ground glass stoppers with methylene chloride and add the rinse to the round bottom flask of the Soxhlet extractor. After

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transferring the XAD-2 resin to the extractor, rinse the XAD-2 module thoroughly into the extractor using a teflon wash bottle containing methylene chloride.

NOTE: Under no circumstances should methanol or acetone be used to transfer the XAD-2 resin.

11.6.1.3 With the XAD-2 resin in the Soxhlet extractor and glass wool on top of the XAD-2 resin, use a clean syringe or volumetric pipet to add a 1-mL aliquot of the internal standard spiking solution (Section 7.2.3.2) to the XAD-2 resin. Be sure that the needle of the syringe penetrates the XAD-2 resin bed to a depth of at least 1.27 cm (0.5 in.). If a laboratory QC sample is being prepared (Section 9.2.4), the XAD-2 resin should be spiked with the PAR spiking solution at this time.

11.6.1.4 Pour approximately 300-400 mL of methylene chloride through the XAD-2 bed so that the round bottom flask is approximately half-full and the XAD-2 bed is covered.

11.6.1.5 Place a heating mantle under the round bottom flask and connect the upper joint of the Soxhlet extractor to a condenser.

NOTE: Start the extraction process immediately after spiking is completed to ensure that no volatilization of organic compounds from the resin or any spiking solutions occurs before the extraction process is started.

11.6.1.6 Allow the sample to extract for at least 16 hours but not more than 24 hours, cycling once every 25-30 minutes.

NOTE: Be sure that cooling water for the condensers is cold and circulating. Watch the extractor through two or three cycles to ensure that the extractor is working properly.

11.6.1.7 After the Soxhlet extractor has been cooled, disconnect the extractor from the condenser and tilt the extractor slightly until the remaining solvent in the Soxhlet has drained into the round bottom flask.

11.6.1.8 Inspect the contents of the round bottom flask to determine whether there is a visible water layer on top of the methylene chloride.

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11.6.1.8.1 If no water layer is observed, transfer the extract through a clean filter into a 500-mL amber glass bottle with PTFE-lined screw cap for subsequent combination with the back-half rinse.

11.6.1.8.2 If a water layer is observed in the Soxhlet round bottom flask, transfer the contents to a separatory funnel through a clean filter, rinsing the round bottom flask three times with methylene chloride and adding the rinsings to the separatory funnel. Drain the methylene chloride from the separatory funnel and store in a clean amber glass bottle. Extract the aqueous layer using a C_{18} SPE column, as described in Section 11.6.3.

11.6.1.9 Archive the extracted XAD-2 resin at <4°C until the HRGC/HRMS analysis is completed.

11.6.1.10 Proceed to Section 11.7.1 for water removal.

11.6.2 Back Half Acetone/Methylene Chloride Rinses (Container No. 4) and Impinger Acetone/Methylene Chloride Rinses (Container No. 6)

The back half solvent rinses (Container No. 4) and the impinger solvent rinses (Container No. 6) are not extracted, but are combined during the water removal process, described in Section 11.7.2.

11.6.3 Impinger Water Contents (Container No. 5)

11.6.3.1 Extract the impinger water using solid phase extraction (SPE). Prepare the SPE cartridge by placing the SPE cartridge in a vacuum manifold. Condition the cartridge with 15-mL aliquots of methylene chloride, methanol, and deionized water. Do not allow the cartridge to go dry from this point until the extraction is completed.

11.6.3.2 Allow the aqueous sample to equilibrate for approximately 30 minutes to settle the suspended particles, if present. Allow the sample to be pulled through the SPE cartridge. Adjust the vacuum to complete the extraction in no less than 15 minutes. An additional SPE cartridge may be used if clogging prevents sufficient sample throughput.

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Before all of the sample has been pulled through the cartridge, add approximately 20 mL of reagent water to the sample bottle, swirl to suspend the solids (if present), and pour into the second reservoir. Pull the remaining sample through the SPE cartridge. Use additional reagent HPLC water rinses until all solids are removed.

Before all of the sample and rinses have been pulled through the cartridge, rinse the sides of the reservoir with small portions of reagent HPLC water. Dry the cartridges under vacuum for 2 hours.

11.6.3.3 Release the vacuum, remove the reservoir from the vacuum manifold, and discard the extracted aqueous solution. Insert a clean vial for eluant collection into the manifold. Each vial should have sufficient capacity to contain the total volume of the elution solvent (approximately 12 mL) and should fit around the drip tip. The drip tip should protrude into the vial to preclude loss of sample from spattering when vacuum is applied. Reassemble the vacuum manifold.

11.6.3.4 Wet each cartridge with 6 mL of acetone. Allow the solvent to soak the C_{18} beads 15-20 seconds. Pull all of the solvent through the cartridges into the vials. Wet each cartridge with 6 mL of methylene chloride. Allow the solvent to soak the C_{18} beads 15-20 seconds. Pull all of the solvent through the cartridge into the vial.

Release the vacuum, remove the vial containing the sample solution. Add 10 g of Na_2SO_4 to the extract; allow the extract to set for 10 minutes; then filter the extract.

11.6.3.5 Proceed to Section 11.7.2 for back half water removal.

11.7 Back Half Sample Water Removal

Water is removed from the XAD-2 extract, the back half and impinger solvent rinses, and the impinger water extract using sodium sulfate. During the drying procedure, the extracts are combined into a Kuderna-Danish setup.

11.7.1 XAD-2 Extract (See Section 11.6.1.10)

11.7.1.1 Prepare a Na_2SO_4 funnel, as described in Sections 11.2.1.2-11.2.1.3.

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11.7.1.2   Place the funnel exit into a clean KD concentrator consisting of a 20 mL concentrator tube connected to a 500 mL evaporative flask. Slowly pour the XAD-2 extract through the Na_2SO_4. Rinse the container containing the extract/Na_2SO_4 three times, using approximately 10 mL of methylene chloride each time. Add rinses to the funnel. Rinse the Na_2SO_4 with approximately 5 mL of methylene chloride to complete the transfer.

Note: Monitor the condition of the Na_2SO_4 as noted in Section 11.2.1.4.

11.7.1.3   Reduce volume of extract to <10 mL, following the K-D concentration procedures described in Sections 11.3.1 and 11.3.2.

11.7.2   Back Half and Impinger Solvent Rinses, and Impinger Water Combined Extract

11.7.2.1   Prepare a Na_2SO_4 funnel, as described in Sections 11.2.1.2-11.2.1.3.

11.7.2.2   Place the funnel into the same 500 mL evaporative flask described in Section 11.7.1.2.

11.7.2.3   Slowly pour the impinger water extract (Section 11.6.3.5) through the Na_2SO_4. Rinse the container containing the extract three times, using approximately 10 mL of methylene chloride each time. Add rinses to the funnel. Rinse the Na_2SO_4 with approximately 5 mL of methylene chloride to complete the transfer.

Note: Monitor the condition of the Na_2SO_4 as noted in Section 11.2.1.4.

11.7.2.4   Slowly pour the combined back half and impinger solvent rinses (Section 11.6.2) through the Na_2SO_4. Rinse the containers containing the rinses three times, using approximately 10 mL of methylene chloride each time. Add rinses to the funnel. Rinse the Na_2SO_4 with approximately 5 mL of methylene chloride to complete the transfer.

Note: Monitor the condition of the Na_2SO_4 as noted in Section 11.2.1.4.

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11.7.2.5 If the volume of the extract is greater than 500 mL, follow the procedures described in Sections 11.2.1.5 and 11.2.1.6.

11.7.2.6 Proceed to Section 11.8 for back half sample concentration.

11.8 Back Half Combined XAD-2 Extract, Back Half and Impinger Solvent Rinses, and Impinger Water Extract Sample Reduction.

The combined XAD-2 extract, back half and impinger rinses, and impinger water extract sample is reduced in volume using macro and micro Kuderna-Danish (K-D) apparatus, and half of the total extract is archived. The other half of the total extract is cleaned according to the procedures described in Section 11.9.

11.8.1 Follow the concentration procedures described in Sections 11.3.1 and 11.3.2.

11.8.2 Transfer the combined, concentrated extract to a calibrated vial or a volumetric flask, rinse the concentrator tube with a minimum volume of methylene chloride and add rinses to the vial, and add methylene chloride, if necessary, to attain a final volume of 10 mL.

11.8.3 Transfer 5.0 mL of the extract to a 10-mL glass storage vial with a PTFE-lined screw cap. Label the extract as "Archived Extract of Back Half", store at <0°C. Mark the liquid level on the vial with a permanent marker to monitor solvent evaporation during storage.

11.8.4 Place the remaining 5.0 mL of the extract through the sample cleanup procedure described in Section 11.9.

11.9 Back Half Combined Sample Cleanup

The un-archived portion of the back half extract is cleaned using acid and base partitioning, and silica gel and carbon column chromatography.

11.9.1 Acid and Base Partitioning (see Section 11.4.1)

11.9.2 Silica Gel Column Chromatography (follow procedure described in Section 11.4.2)

11.9.3 Carbon Column Chromatography (follow procedure described in Section 11.4.3)

11.10 Back Half Combined Sample Concentration to Final Volume

The extract is concentrated to final volume, and the recovery standards are added.

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11.10.1 The extract is concentrated in a calibrated microtube to a final volume of 20 μL to 1 mL, per the analyst's discretion, under a gentle stream of nitrogen.

11.10.2 Add 10 μL of the appropriate recovery standard solution (Section 7.2.5) to the sample extract.

11.10.3 Proceed to Section 11.11 for HRGC/HRMS analysis.

11.11 HRGC/HRMS Sample Analysis

The operation of the HRGC/HRMS instrumentation is verified, and the separate front half and back half extracts are analyzed.

11.11.1 Establish the operating conditions given in Section 10.1, perform initial calibration if necessary (Section 10.2), or verify calibration (Section 10.3).

11.11.2 If an extract is to be reanalyzed and evaporation has occurred, do not add more recovery standard solution. Rather, bring the extract back to its previous volume (e.g., 19 μL, or 18 μL if 2 μL injections are used) with pure nonane.

11.11.3 Inject 1.0 or 2.0 μL of the concentrated extract containing the recovery standard solution, using on-column or splitless injection. The volume injected must be identical to the volume used for calibration (Section 10.1.3.1). Start the HRGC column initial isothermal hold upon injection. Start HRMS data collection after the solvent peak elutes. Stop data collection after the $^{13}C_{12}$-PCB 209 has eluted. Return the column to the initial temperature for analysis of the next extract or standard.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Qualitative Determination

A PCB or labeled compound is identified in a standard, blank, or sample when all of the criteria in Sections 12.1.1 through 12.1.4 are met. If the criteria for identification in Sections 12.1.1-12.1.4 are not met, the PCB analyte has not been positively identified. If interferences preclude identification, an estimated maximum possible concentration (EMPC) can be reported (Section 12.2.6), or options for further cleanup can be explored depending on specific project requirements.

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12.1.1 The signals for the two exact m/z's in Table 6 must be present and must maximize within the same two seconds.

12.1.2 The signal-to-noise ratio (S/N) for the GC peak at each exact m/z must be greater than or equal to 2.5 for each PCB analyte detected in a sample extract, and greater than or equal to 10 for all PCB analytes in the calibration standard (Section 7.2.6).

12.1.3 The ratio of the integrated areas of the two exact m/z's specified in Table 6 must be within the limit in Table 7, or within ±10 percent of the ratio in the midpoint (CS3) calibration or calibration verification (VER), whichever is most recent.

12.1.4 The relative retention time of the peak for a toxic PCB analyte must be within ±15 seconds of the retention times obtained during calibration.

12.2 -- Quantitative Determination

12.2.1 For gas chromatographic peaks that have met the criteria outlined in Section 12.1, calculate the concentration of the PCB compounds in the extract, using the formula:

$$C_x = \frac{A_x \times Q_{is}}{A_{is} \times \overline{RF_n} \times W_s}$$

where:

C_x = *concentration of unlabeled PCB congeners in the front half or back half extract (pg/dscm),*

A_x = *sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and 6) for unlabeled PCBs,*

A_{is} = *sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and 6) for the labeled internal standards,*

Q_{is} = *quantity, in pg, of the internal standard added to the sample before extraction,*

$\overline{RF_n}$ = *calculated mean relative response factor for the analyte (RF_x with n=1 to 13; Section 10.2.1),*

W_s = *volume of air sampled (dscm).*

12.2.2 Concentration in Emission Sample

The total concentration of a native PCB analyte in an emission sample is computed by summing the concentration of the front half and the back half, as follows:

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$$Concentration\ in\ emission\ sample\ (pg/dscm)\ =\ C_{fh}\ +\ C_{bh}$$

where:

C_{fh} = *Concentration of the compound in the front half (pg/dscm), calculated per Section 12.2.1.*
C_{bh} = *Concentration of the compound in the back half (pg/dscm), calculated per Section 12.2.1.*

12.2.3   Calculate the percent recovery of the internal standards measured in the sample extract, using the formula:

$$Percent\ recovery\ =\ \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs} \times RF_{is}} \times 100$$

where:

A_{is} = *sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and 6) for the labeled internal standard,*
A_{rs} = *sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and 6) for the labeled recovery standard,*
Q_{is} = *quantity, in pg, of the internal standard added to the sample before extraction,*
Q_{rs} = *quantity, in pg, of the recovery standard added to the cleaned-up sample residue before HRGC/HRMS analysis, and*
$\overline{RF}_{is}$ = *calculated mean relative response factor for the labeled internal standard relative to the appropriate recovery standard. This represents the mean obtained in Section 10.2.2 (RF_{is} with is = 14 to 23, Table 3).*

Calculate the percent recovery of the cleanup standard similarly. The percent recovery should meet the criteria shown in Table 5. If recoveries are outside the limits of Table 5, the data should be flagged and the impact on reported results discussed in the final report.

12.2.4   Outside Calibration Range

12.2.4.1 If the SICP area at either quantitation m/z for any compound exceeds the calibration range of the system, the extract must be diluted and re-analyzed.

12.2.4.2 Dilute the sample extract by a factor of 10, adjust the concentration of the recovery standard to 100 pg/µL in the extract, and analyze an aliquot of this diluted extract.

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12.2.5   Estimated Detection Limit (EDL)

$$EDL = \frac{2.5\,(H1_S + H2_S)\,(Q_{iS})}{(H1_{is} + H2_{is})\,(RF_n)\,(W_S)}$$

where:

$H1_s$ and $H2_s$ =   *heights of the noise where the primary and secondary m/z's for the PCBs would elute,*

$H1_{is}$ and $H2_{is}$ =   *heights of the response of the primary and secondary m/z's for the internal standard,*

And Q_{is}, $\overline{RF}_n$, and W_s are as described in Section 12.2.1.

12.2.6   Estimated Maximum Possible Concentration (EMPC)

When the response of a signal having the same retention time as a toxic PCB congener has a S/N in excess of 2.5 but does not meet all of the other qualitative identification criteria listed in Section 12.1 calculate the Estimated Maximum Possible Concentration (EMPC). EMPC is calculated using the expressions in Section 12.2.1, except that A_x should represent the sum of the area under the smaller peak and of the other peak area calculated using the theoretical chlorine isotope ratio. The value shall be noted as EMPC and the results reported.

12.2.7   Reporting Units and Levels

Results are reported to three significant figures for the PCBs and labeled compounds found in all standards, blanks, and samples.

12.2.7.1   Air Emission Samples—Analytical results are reported in pg/FH or BH fraction, and are not to be corrected for field, reagent, or laboratory method blanks.

12.2.7.2   Train or Proof Blanks—Results are reported in pg/FH or BH fraction, and are not to be corrected for field, reagent, or laboratory method blanks.

12.2.7.3   Dilutions (Section 12.2.4.2)

Results for PCBs in samples that have been diluted: for this EPA project, both the undiluted and diluted PCB results are to be reported, whether or not all of the analytes are within the calibration range.

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12.2.7.4 Non-Detects

Note the non-detected PCBs as ND and report the estimated detection limit established during the analysis.

13.0 METHOD PERFORMANCE

13.1 In a limited single laboratory demonstration of this method using simulated emission samples, estimated detection limits of approximately 75 pg/sample were achieved for pentachlorinated biphenyl (PeCB); 5 pg/sample for hexachlorinated biphenyl (HxCB); and 25 pg/sample for heptachlorinated biphenyl (HpCB).

13.2 Interlaboratory testing of this method to determine overall precision and bias has not been performed.

14.0 POLLUTION PREVENTION

This method uses solid phase extraction (SPE) techniques for the extraction of PCBs from liquid matrices. SPE uses much less solvent, than traditional liquid-liquid extraction techniques.

15.0 WASTE MANAGEMENT

PCB waste should be disposed of according to Toxic Substances Control Act (TSCA) guidelines 40CFR 700-789, and hazardous waste should be disposed of according to Resource Conservation and Recovery Act (RCRA) guidelines 40CFR 260-269.

16.0 REFERENCES

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17.0   TABLES AND FIGURES

Table 1.   Toxic Polychlorinated Biphenyls Determined by High Resolution Gas Chromatography (HRGC)/High Resolution Mass Spectrometry (HRMS)

PCB[1]	Native compound CAS Registry No.	IUPAC No.[2]
Target Analytes		
3,3',4,4'-TCB	32598-13-3	77
2,3,3',4,4'-PeCB	32598-14-4	105
2,3,4,4',5-PeCB	74472-37-0	114
2,3',4,4',5-PeCB	31508-00-6	118
2',3,4,4',5-PeCB	65510-44-3	123
3,3',4,4',5-PeCB	57465-28-8	126
2,3,3',4,4',5-HxCB	38380-08-4	156
2,3,3',4,4',5'-HxCB	69782-90-7	157
2,3',4,4',5,5'-HxCB	52663-72-6	167
3,3',4,4',5,5'-HxCB	32774-16-6	169
2,2',3,3',4,4',5-HpCB	35065-30-6	170
2,2',3,4,4',5,5'-HpCB	35065-29-3	180
2,3,3',4,4',5,5'-HpCB	39635-31-9	189
Internal Standards		
3,3',4,4'-TCB	160901-67-7	77L
2,3,3',4,4'-PeCB	160901-70-2	105L
2,3,4,4',5-PeCB	160901-72-4	114L
2,3',4,4',5-PeCB	160901-73-5	118L
2',3,4,4',5-PeCB	160901-74-6	123L
3,3',4,4',5-PeCB	160901-75-7	126L
2,3,3',4,4',5-HxCB	160901-77-9	156L
2,3,3',4,4',5'-HxCB	160901-78-0	157L
2,3',4,4',5,5'-HxCB	161627-18-5	167L
3,3',4,4',5,5'-HxCB	160901-79-1	169L
2,2',3,3',4,4',5-HpCB	160901-80-4	170L
2,2',3,4,4',5,5'-HpCB	160901-82-6	180L
2,3,3',4,4',5,5'-HpCB	160901-83-7	189L
Surrogate Standards		
$^{13}C_{12}$-3,4,4',5-TCB	160901-68-8	81
$^{13}C_{12}$-2,3,3',5,5'-PeCB	160901-71-3	111
Recovery Standards		
$^{13}C_{12}$-2,2',5,5'-TCB	160901-66-6	52
$^{13}C_{12}$-2,2',4,4',5-PeCB	160901-69-9	101
$^{13}C_{12}$-2,2',3,4,4',5'-HxCB	160901-76-8	138
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB	160901-81-5	178
Final Eluter Standard		
$^{13}C_{12}$-DCB	160901-84-8	209

[1] Polychlorinated biphenyls:

    TCB = Tetrachlorobiphenyl
    PeCB = Pentachlorobiphenyl
    HxCB = Hexachlorobiphenyl
    HpCB = Heptachlorobiphenyl
    DCB = Decachlorobiphenyl

[2] Suffix "L" designates a labeled compound.

Table 2. Retention Time (RT) References, Quantitation References, and Retention Times (RTs) for the Toxic PCBs

IUPAC No.[1]	PCB congener	IUPAC No.[1]	Retention time and quantitation reference	RT[2] (min)
52L	13C12-2,2',5,5'-TCB	—[3]	13C12-2,2',5,5'-TCB	28.66
81L	13C12-3,4,4',5-TCB[4]	52L	13C12-2,2',5,5'-TCB	37.89
77L	13C12-3,3',4,4'-TCB	52L	13C12-2,2',5,5'-TCB	38.85
77	3,3',4,4'-TCB	77L	13C12-3,3',4,4'-TCB	38.85
101L	13C12-2,2',4,5,5'-PeCB	—	13C12-2,2',4,5,5'-PeCB	35.02
111L	13C12-2,3,3',5,5'-PeCB[4]	101L	13C12-2,2',4,5,5'-PeCB	37.13
123	2',3,4,4',5-PeCB	118L	13C12-2,3',4,4',5-PeCB	39.90
118L	13C12-2,3',4,4',5-PeCB	101L	13C12-2,2',4,5,5'-PeCB	40.17
118	2,3',4,4',5-PeCB	118L	13C12-2,3',4,4',5-PeCB	40.17
114	2,3,4,4',5-PeCB	105L	13C12-2,3,3',4,4'-PeCB	40.79
105L	13C12-2,3,3',4,4'-PeCB	101L	13C12-2,2',4,5,5'-PeCB	42.22
105	2,3,3',4,4'-PeCB	105L	13C12-2,3,3',4,4'-PeCB	42.22
126L	13C12-3,3',4,4',5-PeCB	101L	13C12-2,2',4,5,5'-PeCB	44.75
126	3,3',4,4',5-PeCB	126L	13C12-3,3',4,4',5-PeCB	44.75
138L	13C12-2,2',3,4,4',5'-HxCB	—	13C12-2,2',4,5,5'-PeCB	43.23
167L	13C12-2,3',4,4',5,5'-HxCB	138L	13C12-2,2',3,4,4',5'-HxCB	45.72
167	2,3',4,4',5,5'-HxCB	167L	13C12-2,3',4,4',5,5'-HxCB	45.72
156L	13C12-2,3,3',4,4',5-HxCB	138L	13C12-2,2',3,4,4',5'-HxCB	47.37
157L	13C12-2,3,3',4,4',5'-HxCB	138L	13C12-2,2',3,4,4',5'-HxCB	47.79
156	2,3,3',4,4',5-HxCB	156L	13C12-2,3,3',4,4',5-HxCB	47.37
157	2,3,3',4,4',5'-HxCB	157L	13C12-2,3,3',4,4',5'-HxCB	47.79
169L	13C12-3,3',4,4',5,5'-HxCB	138L	13C12-2,2',3,4,4',5'-HxCB	50.25
169	3,3',4,4',5,5'-HxCB	169L	13C12-3,3',4,4',5,5'-HxCB	50.25
178L	13C12-2,2',3,3',5,5',6-HpCB	—	13C12-2,2',4,5,5'-PeCB	42.88
180L	13C12-2,2',3,4,4',5,5'-HpCB	178L	13C12-2,2',3,3',5,5',6-HpCB	47.88
180	2,2',3,4,4',5,5'-HpCB	180L	13C12-2,2',3,4,4',5,5'-HpCB	47.88
170	2,2',3,3',4,4',5-HpCB	180L	13C12-2,2',3,4,4',5,5'-HpCB	49.90
189L	13C12-2,3,3',4,4',5,5'-HpCB	178L	13C12-2,2',3,3',5,5',6-HpCB	52.56
189	2,3,3',4,4',5,5'-HpCB	189L	13C12-2,3,3',4,4',5,5'-HpCB	52.56
209L	13C12-DCB[5]	178L	13C12-2,2',3,3',5,5',6-HpCB	56.63

[1] Suffix "L" indicates labeled compound.
[2] Retention time data are for HT-8 column (per manufacturer).
[3] Absolute recovery standards.
[4] Surrogate standard.
[5] Final eluter.

Table 3. Concentrations of Stock and Spiking Solutions Containing the Native PCBs and Labeled Compounds

Cpd. No.	Compound	m/z type	Stock[3] (ng/mL)	Spiking Solution[2] (ng/mL)	Spiking Level (ng)
	Precision and Recovery Standards[1]				
1	3,3',4,4'-TCB	77	20	0.8	0.8
2	2,3,3',4,4'-PeCB	105	1000	40	40
3	2,3,4,4',5-PeCB	114	1000	40	40
4	2,3',4,4',5-PeCB	118	1000	40	40
5	2',3,4,4',5-PeCB	123	1000	40	40
6	3,3',4,4',5-PeCB	126	100	4	4
7	2,3,3',4,4',5-HxCB	156	1000	40	40
8	2,3,3',4,4',5'-HxCB	157	1000	40	40
9	2,3',4,4',5,5'-HxCB	167	1000	40	40
10	3,3',4,4',5,5'-HxCB	169	200	8	8
11	2,2',3,3',4,4',5-HpCB	170	200	8	8
12	2,2',3,4,4',5,5'-HpCB	180	1000	40	40
13	2,3,3',4,4',5,5'-HpCB	189	200	8	8
	Internal Standards[4]				
14	13C12-3,3',4,4'-TCB	77L	1000	2	2
15	13C12-2,3,3',4,4'-PeCB	105L	1000	2	2
16	13C12-2,3',4,4',5-PeCB	118L	1000	2	2
17	13C12-3,3',4,4',5-PeCB	126L	1000	2	2
18	13C12-2,3,3',4,4',5-HxCB	156L	1000	2	2
19	13C12-2,3,3',4,4',5'-HxCB	157L	1000	2	2
20	13C12-2,3',4,4',5,5'-HxCB	167L	1000	2	2
21	13C12-3,3',4,4',5,5'-HxCB	169L	1000	2	2
22	13C12-2,2',3,4,4',5,5'-HpCB	180L	1000	2	2
23	13C12-2,3,3',4,4',5,5'-HpCB	189L	1000	2	2
	Surrogate/Cleanup Standards[5]				
24	13C12-3,4,4',5-TCB	81L	200	1.0	1.0
25	13C12-2,3,3',5,5'-PeCB	111L	1000	5.0	5.0
	Recovery Standards[6]				
26	13C12-2,2',5,5'-TCB	52L	1000	200	2
27	13C12-2,2',4,5,5'-PeCB	101L	1000	200	2
28	13C12-2,2',3,4,4',5'-HxCB	138L	1000	200	2
29	13C12-2,2',3,3',5,5',6-HpCB	178L	1000	200	2
	Final Eluter				
30	13C12-DCB	209L	2000	8	8

[1] Section 7.2.7-prepared in nonane and diluted to prepare spiking solution.

[2] Sections 7.2.2, 7.2.4., 7.2.5, 7.2.7-prepared in acetone from stock solution daily.

[3] Section 7.2.1-prepared in nonane and diluted to prepare spiking solution. Concentrations are adjusted for expected background levels.

[4] Section 7.2.3 2-prepared in acetone from stock solution daily. Concentrations are adjusted for expected background levels.

[5] Section 7.2.4-prepared in acetone; added to XAD-2 prior to shipment into the field; add to filter before cleanup.

[6] Section 7.2.5-prepared in nonane; added to concentrated extract prior to injection.

Table 4. Concentrations of PCBs in Calibration and Calibration Verification Solutions

	IUPAC No.[1]	CS1 (ng/mL)	CS2 (ng/mL)	CS3[2] (ng/mL)	CS4 (ng/mL)	CS5 (ng/mL)
Precision and Recovery Standards						
3,3',4,4'-TCB	77	0.5	2	10	40	200
2,3,3',4,4'-PeCB	105	2.5	10	50	200	1000
2,3,4,4',5-PeCB	114	2.5	10	50	200	1000
2,3',4,4',5-PeCB	118	2.5	10	50	200	1000
2',3,4,4',5-PeCB	123	2.5	10	50	200	1000
3,3',4,4',5-PeCB	126	2.5	10	50	200	1000
2,3,3',4,4',5-HxCB	156	5	20	100	400	2000
2,3,3',4,4',5'-HxCB	157	5	20	100	400	2000
2,3',4,4',5,5'-HxCB	167	5	20	100	400	2000
3,3',4,4',5,5'-HxCB	169	5	20	100	400	2000
2,2',3,3',4,4',5-HpCB	170	5	20	100	400	2000
2,2',3,4,4',5,5'-HpCB	180	5	20	100	400	2000
2,3,3',4,4',5,5'-HpCB	189	5	20	100	400	2000
Internal Standards						
13C12-3,3',4,4'-TCB	77L	100	100	100	100	100
13C12-2,3,3',4,4'-PeCB	105L	100	100	100	100	100
13C12-2,3',4,4',5-PeCB	118L	100	100	100	100	100
13C12-3,3',4,4',5-PeCB	126L	100	100	100	100	100
13C12-2,3,3',4,4',5-HxCB	156L	100	100	100	100	100
13C12-2,3,3',4,4',5'-HxCB	157L	100	100	100	100	100
13C12-2,3',4,4',5,5'-HxCB	167L	100	100	100	100	100
13C12-3,3',4,4',5,5'-HxCB	169L	100	100	100	100	100
13C12-2,2',3,4,4',5,5'-HpCB	180L	100	100	100	100	100
13C12-2,3,3',4,4',5,5'-HpCB	189L	100	100	100	100	100
Surrogate Standards						
13C12-3,4,4',5-TCB	81L	0.5	2	10	40	200
13C12-2,3,3',5,5'-PeCB	111L	2.5	10	50	200	1000
Recovery Standards						
13C12-2,2',5,5'-TCB	52L	100	100	100	100	100
13C12-2,2',4,5,5'-PeCB	101L	100	100	100	100	100
13C12-2,2',3,4,4',5'-HxCB	138L	100	100	100	100	100
13C12-2,2',3,3',5,5',6-HpCB	178L	100	100	100	100	100
Final Eluter						
13C12-DCB	209L	200	200	200	200	200

[1] Suffix "L" indicates labeled compound.
[2] Sections 7.2.6, calibration verification solution.

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Table 5. Labeled Compound Target PCB Recoveries

Labeled PCB	IUPAC No.	Test conc (ng/mL)[1]	Labeled compound recovery	
			(ng/mL)	(%)
Internal Standards				
13C12-3,3',4,4'-TCB	77	100	30-150	30-150
13C12-2,3,3',4,4'-PeCB	105	100	30-150	30-150
13C12-2,3',4,4',5-PeCB	118	100	30-150	30-150
13C12-3.3',4,4',5-PeCB	126	100	30-150	30-150
13C12-2,3,3',4,4',5-HxCB	156	100	30-150	30-150
13C12-2,3,3',4,4',5'-HxCB	157	100	30-150	30-150
13C12-2,3',4,4',5,5'-HxCB	167	100	30-150	30-150
13C12-3,3',4,4',5,5'-HxCB	169	100	30-150	30-150
13C12-2,2',3,4,4',5,5'-HpCB	180	100	30-150	30-150
13C12-2,3,3',4,4',5,5'-HpCB	189	100	30-150	30-150
Surrogate Standards				
13C12-3,4,4',5-TCB	81	50	5-75	10-150
13C12-2,3,3',5,5'-PeCB	111	250	50-325	20-130

[1] Based on 20 μL final extract volume.

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Table 6. Descriptors, Exact m/z's, m/z Types, and Elemental Compositions of the PCBs

Descriptor	Exact m/z[1]	m/z type	Elemental composition	Substance[2]
1.	289.9224	M	C12 H6 35Cl4	TCB
	291.9194	M+2	C12 H6 35Cl3 37Cl	TCB
	301.9626	M	13C12 H6 35Cl4	TCB[3]
	303.9597	M+2	13C12 H6 35Cl3 37Cl	TCB[3]
	318.9792	Lock Mass	—	PFK
	325.8804	M+2	C12 H5 35Cl4 37Cl	PeCB
	327.8775	M+4	C12 H5 35Cl3 37Cl2	PeCB
	330.9793	Lock Mass Check	—	PFK
	337.9207	M+2	13C12 H5 35Cl4 37Cl	PeCB[3]
	339.9178	M+4	13C12 H5 35Cl3 37Cl2	PeCB[3]
2.	325.8804	M+2	C12 H5 35Cl4 37Cl	PeCB
	327.8775	M+4	C12 H5 35Cl3 37Cl2	PeCB
	337.9207	M+2	13C12 H5 35Cl4 37Cl	PeCB[3]
	339.9178	M+4	13C12 H5 35Cl3 37Cl2	PeCB[3]
	354.9792	Lock Mass	—	PFK
	354.9792	Lock Mass Check	—	PFK
	393.8025	M+2	C12 H3 35Cl6 37Cl	HpCB
	395.7996	M+4	C12 H3 35Cl5 37Cl2	HpCB
	405.8428	M+2	13C12 H3 35Cl6 37Cl	HpCB[3]
	407.8398	M+4	13C12 H3 35Cl5 37Cl2	HpCB[3]
3.	359.8415	M+2	C12 H4 35Cl5 37Cl	HxCB
	361.8385	M+4	C12 H4 35Cl4 37Cl2	HxCB
	371.8817	M+2	13C12 H4 35Cl5 37Cl	HxCB[3]
	373.8788	M+4	13C12 H4 35Cl4 37Cl2	HxCB[3]
	380.9760	Lock Mass	—	PFK
	380.9760	Lock Mass Check	—	PFK
	393.8025	M+2	C12 H3 35Cl6 37Cl	HpCB
	395.7996	M+4	C12 H3 35Cl5 37Cl2	HpCB
	405.8428	M+2	13C12 H3 35Cl6 37Cl	HpCB[3]
	407.8398	M+4	13C12 H3 35Cl5 37Cl2	HpCB[3]
4.	504.9696	Lock Mass	—	PFK
	504.9696	Lock Mass Check	—	PFK
	509.7229	M+4	13C12 35Cl8 37Cl2	DCB[3]
	511.7199	M+6	13C12 35Cl7 37Cl3	DCB[3]

[1] Nuclidic masses used were:

H = 1.007825   C = 12.00000

13C = 13.003355   35Cl = 34.968853   37Cl = 36.965903

[2] TCB = Tetrachlorobiphenyl

PeCB = Pentachlorobiphenyl

HxCB = Hexachlorobiphenyl

HpCB = Heptachlorobiphenyl

DCB = Decachlorobiphenyl.

[3] 13C labeled compound.

Table 7. Theoretical Ion Abundance Ratios and QC Limits

Chlorine atoms	m/z's forming ratio	Theoretical ratio	QC Limit[1]	
			Lower	Upper
4	M/(M+2)	0.77	0.65	0.89
5	(M+2)/(M+4)	1.55	1.32	1.78
6	(M+2)/(M+4)	1.24	1.05	1.43
7	(M+2)/(M+4)	1.05	0.88	1.20
10	(M+4)/(M+6)	1.17	0.99	1.35

[1] QC limits represent +/- 15 percent windows around the theoretical ion abundance ratio. These limits are preliminary.

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Table 8. GC Retention Time Window Defining Solution and Congener Specificity Test Standard[1] (Section 7.2.8)

Congener group	First eluted		Last eluted	
TCB	54	2,2',6,6'	77	3,3',4,4'
PeCB	104	2,2',4,6,6'	126	3,3',4,4',5
HxCB	155	2,2',4,4',6,6'	169	3,3',4,4',5,5'
HpCB	188	2,2',3,4',5,6,6'	189	2,3,3',4,4',5,5'

Resolution test compounds

123	2',3,4,4',5-PeCB	156	2,3,3',4,4',5-HxCB
118	2,3',4,4',5-PeCB	157	2,3,3',4,4',5'-HxCB

[1] All compounds are at a concentration of 100 ng/mL in nonane.

Appendix A

Recommended XAD-2 Resin Cleaning and Pre-Spiking Procedures

A-1
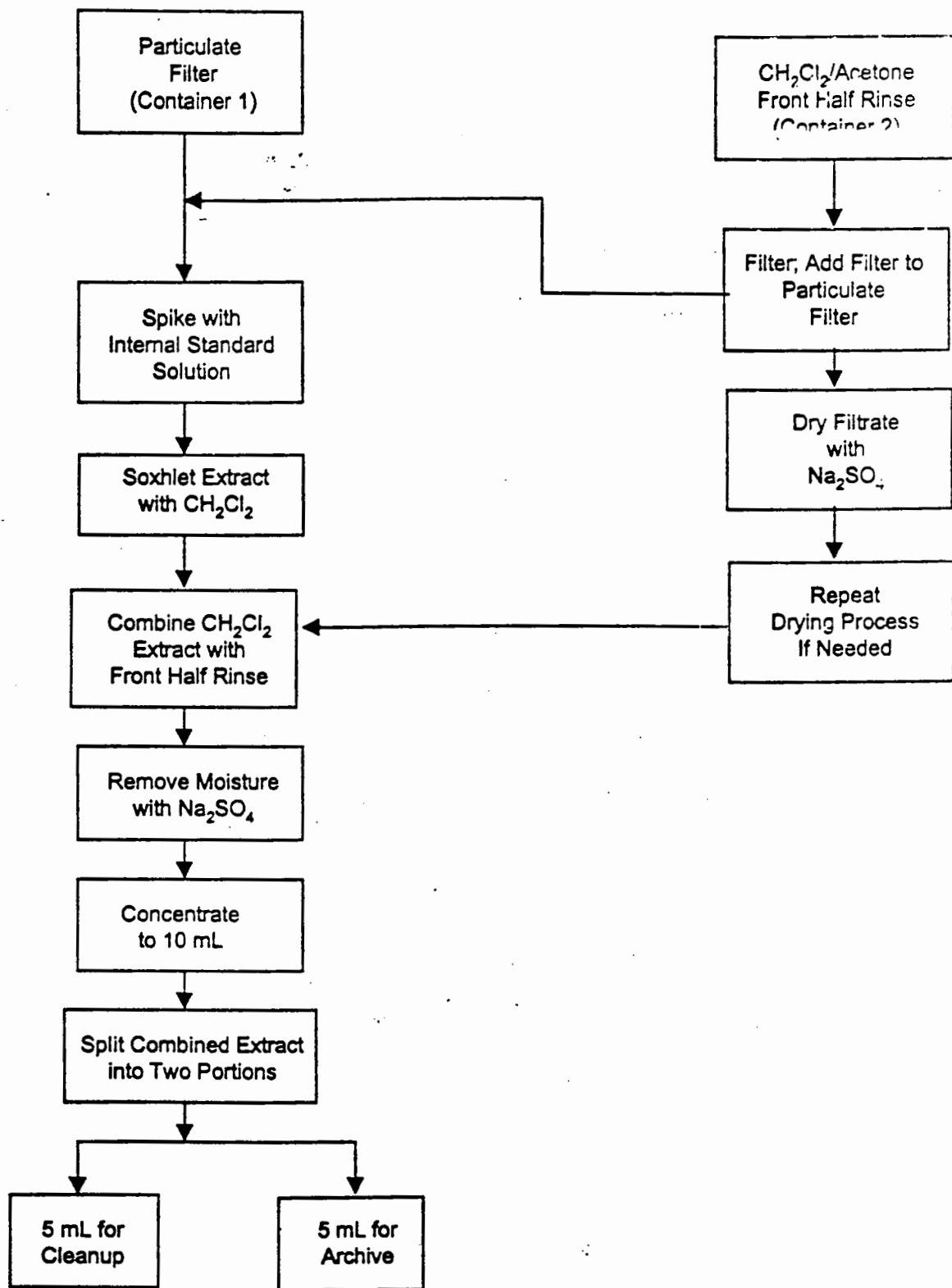
Figure 1. Sample Extraction Procedure for Stationary Source Emission Sample (Front Half Sample Fraction)
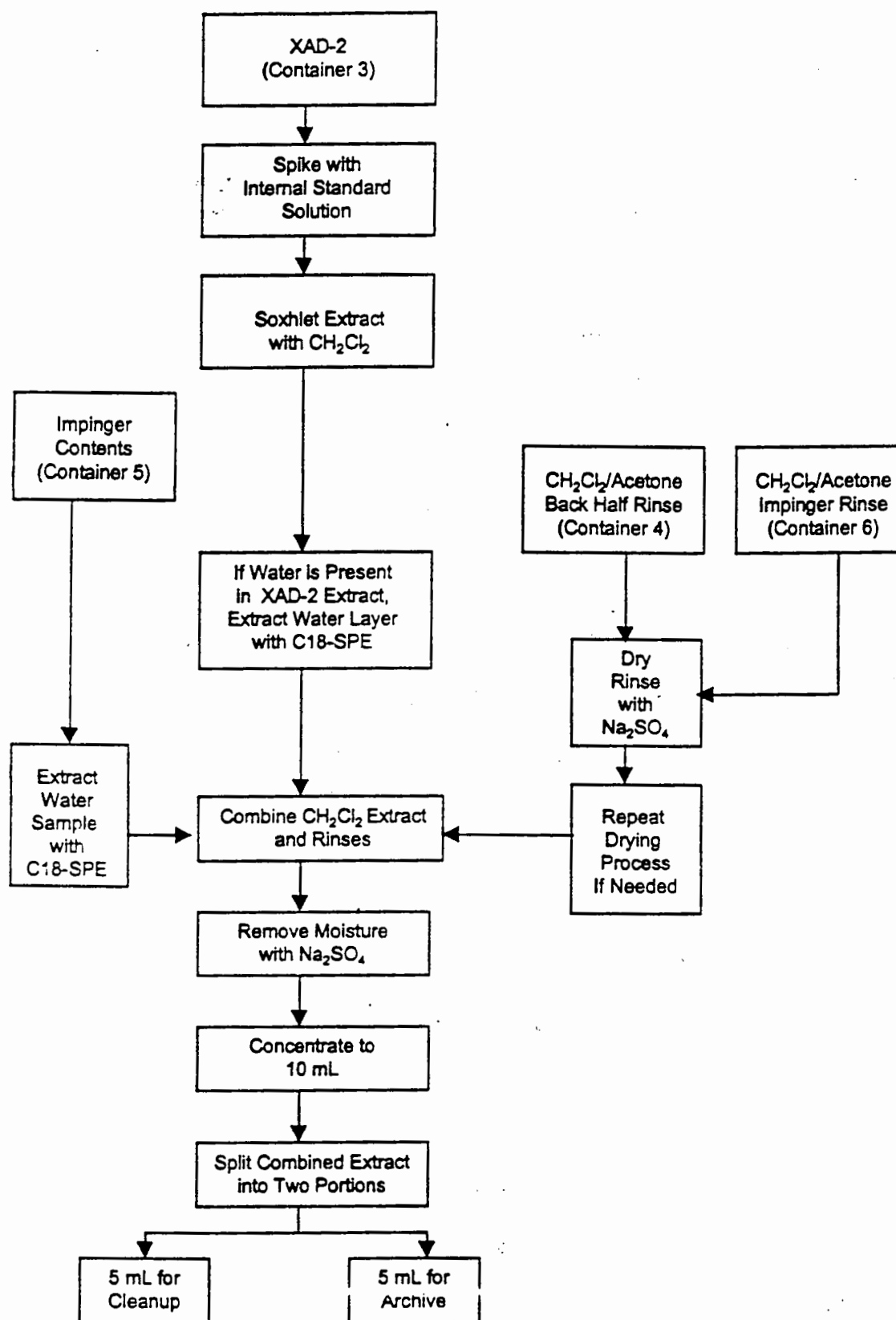
Figure 1. (Continued - Back Half Sample Fraction)

```
                    ┌──────────────┐
                    │   Extract    │
                    │   Cleanup    │
                    └──────┬───────┘
                           ▼
                 ┌──────────────────┐
                 │ Solvent Exchange │
                 │   into Hexane    │
                 └────────┬─────────┘
                          ▼
                 ┌──────────────────┐
                 │ Spike Surrogate  │
                 │ Standard Solution*│
                 └────────┬─────────┘
                          ▼
                 ┌──────────────────┐
                 │Extract Hexane Extract│
                 │ with Sulfuric Acid │
                 └────────┬─────────┘
              ┌───────────┴────────────┐
              ▼                        ▼
      ┌──────────────┐        ┌──────────────────┐
      │ Discard the  │        │ Wash the Hexane  │
      │Aqueous Layer │        │   Layer with     │
      └──────────────┘        │   NaCl Solution  │
                              └────────┬─────────┘
                        ┌──────────────┴───────────┐
                        ▼                          ▼
                ┌──────────────┐          ┌──────────────────┐
                │ Discard the  │          │ Extract the Hexane│
                │Aqueous Layer │          │      with          │
                └──────────────┘          │   KOH Solution     │
                                          └────────┬─────────┘
                                  ┌────────────────┴──────────┐
                                  ▼                           ▼
                          ┌──────────────┐          ┌──────────────────┐
                          │ Discard the  │          │ Wash the Hexane  │
                          │Aqueous Layer │          │ Layer with NaCl  │
                          └──────────────┘          │    Solution      │
                                                    └────────┬─────────┘
                                          ┌──────────────────┴────────┐
                                          ▼                           ▼
                                  ┌──────────────┐          ┌──────────────────┐
                                  │ Discard the  │          │      Dry         │
                                  │Aqueous Layer │          │ Extract with     │
                                  └──────────────┘          │    Na2SO4        │
                                                            └────────┬─────────┘
                                                                     ▼
                                                            ┌──────────────┐
                                                            │  Silica Gel  │
                                                            │   Cleanup    │
                                                            └──────┬───────┘
                                                                   ▼
                                                            ┌──────────────┐
                                                            │ Carbon Column│
                                                            │   Cleanup    │
                                                            └──────┬───────┘
                                                                   ▼
                                                            ┌──────────────┐
                                                            │  Concentrate │
                                                            │ PCB Fraction │
                                                            └──────┬───────┘
                      ┌──────────────┐                             ▼
                      │  HRGC/HRMS   │◄───────────────────┌──────────────────┐
                      │   Analyses   │                    │  Add Recovery    │
                      └──────────────┘                    │ Standard Solution│
                                                          └──────────────────┘
```

* The surrogate standard solution
is not added to the XAD-2 back half rinse
extract because these surrogates are used
in pre-sampling spike of XAD-2.

Figure 2. Extract Cleanup Procedure

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XAD-2 Resin Cleaning Procedure

Pre-cleaned XAD-2 resin (Supelco) is extracted in methylene chloride for at least 24 hours and dried using high-purity nitrogen. The extraction procedure is performed in a large Soxhlet extractor, which will contain approximately 100 g of Amberlite XAD-2. Multiple Soxhlet extraction setups may be employed, depending upon the number of XAD-2 traps needed. The resin must be carefully retained between two glass wool plugs inside the Soxhlet extractor, because it floats on methylene chloride. The XAD-2 resin is dried by placing the extracted resin (~200 g) in a Pyrex column (10 cm x 40 cm). The drying column has sufficient space for fluidizing the XAD-2 bed, while generating a minimum resin load at the exit of the column. The nitrogen was purified by passing it through a charcoal trap between the nitrogen cylinder (size 1A) and the column. The rate of nitrogen flow (ca 40 L/min) through the column should be set to agitate the bed gently to remove the residual solvent.

Storage of Clean XAD-2 Resin

XAD-2 resin cleaned and dried as prescribed above is suitable for immediate use in the field, provided it passes the QC contamination check described below. However, precleaned dry XAD-2 resin may develop unacceptable levels of contamination if stored for periods exceeding one month. If precleaned XAD-2 resin is not to be used immediately, it should be stored in a clean jar that is sealed with Teflon tape. An aliquot shall then be taken for the QC contamination check for determining the background levels of target analytes.

If the stored resin fails the QC check, it may be recleaned by repeating the methylene chloride extraction described above. The QC contamination check shall be repeated after the resin is recleaned and dried.

QC Contamination Check of XAD-2 Resin

The XAD-2 resin shall be subjected to a QC check to confirm the absence of any contaminants that might cause interferences in the subsequent analysis of field samples. An aliquot of resin, equivalent in size (~40 g) to one XAD-2 module charge, shall be used to check a single batch of resin for its quality control.

The XAD-2 resin aliquot shall be subjected to the same extraction, concentration, cleanup, and analytical procedures as those applied to the field samples. The quantitative criteria for acceptable resin quality will depend on the detection limit criteria established for the field sampling and analysis program.

Resin which yields a background or blank value equal to or greater than that corresponding to the levels of concern for the analyte(s) shall be rejected for field use. Note that the acceptance limit for resin cleanliness depends not only on the inherent detection limit of the analysis

A-2

method but also on the expected field sample volume and on the desired limit of detection in the sampled stream.

Pre-Sampling Surrogate Spike

Prepare the Surrogate Spike solution as described in Section 7.2.4 of this method. The XAD-2 sampling module (trap) has sealed ball and socket joints and is wrapped in pre-muffled aluminum foil and bubble wrap. The technician must wear clean cotton or nylon gloves prior to opening the sealed joints. The teflon tape and clamp on the exit end are removed, and the trap carefully unwrapped. The foil is then placed on a clean, stable flat surface with the clean side, the inner surface, facing up. The trap is placed on the foil with the open end toward the technician.

The technician must prerinse a syringe six to eight times with methylene chloride. The syringe volume should be as close as possible to the volume of spiking solution to be added. The syringe is then placed on the clean foil alongside the trap. The clean syringe is then used to withdraw 1 mL of the surrogate spike solution. The needle is positioned at the center of the glass wool plug and inserted through the glass wool and into approximately one centimeter of the XAD-2 resin. The needle should be in the resin, not between the resin and glass wall. The syringe contents are injected and the syringe withdrawn. The trap is then sealed and placed in $\leq 0°C$ for storage. The syringe is rinsed again several times with dichloromethane to clean the spiking solution from it. The gloves are discarded and a fresh pair is used for spiking the second or next trap. The spiked traps will then be packed with dry ice and sent to the field for sampling.

The date of spiking, identity of the XAD-2 module, identity and volume of the spiking solution used, and the name of the technician who performed the spiking are recorded in the study laboratory record book.

A-3

Appendix B
Recommended Procedure for Cleaning the Particulate Filter

B-1

Recommended Procedure For Cleaning the Filter

Prior to use in the field, each lot of filters shall be subjected to precleaning and a quality control or contaminantion check to confirm that there are no contaminants present that will interfere with the analysis of selected species at the target detection limits.

Filters will be precleaned by placing in a muffle oven at >400°C for 12-16 hours. As a QC check, a filter will be extracted, and subjected to the same concentration, clean-up and analysis precedures to be used for the field samples.

The quantitative criterion for acceptable filter quality will depend on the detection limit criteria established for the field sampling and analysis program. Filters that give a background or blank signal per filter greater than or equal to the target detection limit for the analyte(s) of concern shall be rejected for field use. Note that acceptance criteria for filter cleanliness depend not only on the inherent detection limit of the analysis method but also on the expected field sample volume and on the desired limit of detection in the sampled stream.

If the filters do not pass the QC check, they shall be re-muffled, re-extracted, and re-analyzed until an acceptably low background level is achieved.

N-1-2
Draft Sewage Sludge Method

Proposed Analytical Method for

Determination of Toxic Polychlorinated Biphenyls in
Sewage Sludge using Isotope Dilution High Resolution
Gas Chromatography/High Resolution Mass Spectrometry

July 20, 1999

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Proposed Analytical Method for Determination of Toxic Polychlorinated Biphenyls in Sewage Sludge by Isotope Dilution High Resolution Gas Chromatography/High Resolution Mass Spectrometry

1.0 SCOPE AND APPLICATION

1.1 This analytical method is for determination of the toxic polychlorinated biphenyls (PCBs) in sewage sludge by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The method is for use in the Emission Measurement Center's (EMC) data gathering effort to support a Maximum Achievable Control Technology (MACT) standard to limit emissions of hazardous air pollutants at two sewage sludge incinerators. The method is based on a compilation of methods from the technical literature and EPA Method 1668 (references 1-14).

1.2 The method presented here is intended to determine toxic PCBs in samples containing PCBs as single congeners or as complex mixtures. The target analytes are listed in Table 1.

1.3 The method is restricted for use only by or under the supervision of analysts experienced in the use of high resolution gas chromatography (HRGC)/high resolution mass spectrometry (HRMS), and skilled in the interpretation of mass spectra.

1.4 Because of the extreme toxicity of these compounds, the analyst must take necessary precautions to prevent exposure to himself/herself, or to others, of materials known or believed to contain PCBs.

2.0 SUMMARY OF METHOD

2.1 An analytical flow diagram depicting the sewage sludge extraction procedure is shown in Figure 1. Labeled PCBs are spiked into a well-mixed 2 g aliquot of the wet sludge. Solids are homogenized into a slurry, the slurry is mixed with drying agent, and that mixture is extracted in a Soxhlet apparatus with methylene chloride. The extract is concentrated and spiked with cleanup standards.

2.2 A flow diagram depicting the sewage sludge extract cleanup procedure is shown in Figure 2. The sewage sludge extracts are cleaned using acid and base partitioning, granular copper (for removal of sulfur), and silica gel and activated carbon column chromatography. Oily hydrocarbons are removed using High Performance Liquid Chromatography (HPLC)/Gel Permeation Chromatography (GPC).

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2.3 After cleanup, the extract is concentrated to a final volume between 20 μL - 1.0 mL, per the analyst's discretion. Prior to HRMS/HRGC injection, recovery standards are added to each extract, and an aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a high resolution mass spectrometer. Two exact m/z's are monitored for each analyte.

2.4 An individual PCB congener is identified by comparing the GC retention time and ion-abundance ratio of two exact m/z's with the corresponding retention time of an authentic standard and the theoretical or acquired ion-abundance ratio of the two exact m/z's. Isomer specificity for the toxic PCBs is achieved using GC columns that resolve these congeners from the other PCB analytes. Results are quantified using relative response factors.

2.5 The quality of the analysis is assured through reproducible calibration and verification of operation for the extraction, cleanup, and GC/MS systems.

3.0 DEFINITIONS AND ABBREVIATIONS

3.1 Definitions and Acronyms

3.1.1 **Analyte** – a PCB compound measured by this method. The analytes are listed in Table 1.

3.1.2 **Calibration Standard (CS)** – a solution prepared from a secondary standard and/or stock solutions and used to calibrate the response of the instrument with respect to analyte concentration.

3.1.3 **Calibration Verification Standard (VER)** – the mid-point calibration standard (CS3) that is used to verify calibration (see Table 4).

3.1.4 **Congener** – refers to a particular compound of the same chemical family.

3.1.5 **CS1, CS2, CS3, CS4, CS5** – see calibration standards in Table 4

3.1.6 **Field Blank** – an aliquot of 4% (v/v) HNO_3 acid that is placed in a sample container in the laboratory or the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

3.1.7 **HRGC** – high resolution gas chromatography or gas chromatograph.

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3.1.8   **HRMS** – high resolution mass spectrometry or mass spectrometer.

3.1.9   **Internal Standard (IS)** – a component which is added to every sample and is present in the same concentration in every blank, quality control sample, and calibration solution. The IS is added to the sample before extraction and is used to measure the concentration of the analyte and surrogate compound. The IS recovery serves as an indicator of the overall performance of the analysis.

3.1.10   **K-D** – Kuderna-Danish concentrator; a device used to concentrate the analytes in a solvent.

3.1.11   **Laboratory Blank** – see Laboratory Method Blank.

3.1.12   **Laboratory Method Blank** – an aliquot of reagent water or solvent that is treated exactly as a sample including exposure to all laboratory glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The laboratory method blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

3.1.13   **Laboratory Spike Sample** – a laboratory-prepared matrix blank spiked with known quantities of analytes. The laboratory spike sample is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in the method for precision and recovery.

3.1.14   **May** – this action, activity, or procedural step is neither required nor prohibited.

3.1.15   **May not** – this action, activity, or procedural step is prohibited.

3.1.16   **Must** – this action, activity, or procedural step is required.

3.1.17   **m/z Scale** – the molecular mass to charge ratio scale.

3.1.18   **PAR** – precision and recovery standard; secondary standard used to prepare laboratory spike samples.

3.1.19   **Percent Relative Standard Deviation (%RSD)** – the standard deviation times 100 divided by the mean. Also termed "coefficient of variation."

3.1.20   **PFK** – perfluorokerosene; the mixture of compounds used to calibrate the exact m/z scale in the HRMS.

3.1.21   **Primary Dilution Standard** – a solution containing the specified analytes that is purchased or prepared from stock solutions and diluted as needed to prepare calibration solutions and other solutions.

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3.1.22 **QC Check Sample** – a sample containing all or a subset of the analytes at known concentrations. The QC check sample is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

3.1.23 **Reagent Water** – water demonstrated to be free from the analytes of interest and potentially interfering substances at the analyte estimated detection limit; e.g., HPLC grade water.

3.1.24 **Recovery Standard** – a known amount of component added to the concentrated sample extract before injection. The response of the internal standards relative to the recovery standard is used to estimate the overall recovery of the internal standards.

3.1.25 **Relative Response Factor** – the response of the mass spectrometer to a known amount of an analyte relative to a known amount of an internal standard.

3.1.26 **RF** - response factor (see Section 10.2.2).

3.1.27 **RPD** – relative percent difference, defined as the absolute value of the difference between two values divided by the mean of the two values, expressed as a percentage.

3.1.28 **S/N** – signal to noise ratio.

3.1.29 **Should** – this action, activity, or procedural step is suggested but not required.

3.1.30 **SICP** – selected ion current profile; the line described by the signal at an exact m/z.

3.1.31 **Specific Isomers** – a specific isomer is designated by indicating the exact positions (carbon atoms) where chlorines are located within the molecule For example, 2,3,3',4,4'-PeCB refers to only one of the 209 possible PCB isomers - that isomer which is chlorinated in the 2,3,3',4,4'-position of the biphenyl ring structure.

3.1.32 **Specificity** – the ability to measure an analyte of interest in the presence of interferences and other analytes of interest encountered in a sample.

3.1.33 **Stock Solution** – a solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

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3.1.34 **Toxic PCB** – any or all of the toxic polychlorinated biphenyl isomers shown in Table 1.

3.1.35 **VER** – see Calibration Verification Standard (Section 3.1.3).

3.2 Abbreviations

3.2.1 **PCB** – any or all of the 209 possible polychlorinated biphenyl isomers.

3.2.2 **TCB** – abbreviation for tetrachlorinated biphenyl.

3.2.3 **PeCB** – abbreviation for pentachlorinated biphenyl.

3.2.4 **HxCB** – abbreviation for hexachlorinated biphenyl.

3.2.5 **HpCB** – abbreviation for heptachlorinated biphenyl.

3.2.6 **DCB** – abbreviation for decachlorinated biphenyl.

4.0 CONTAMINATION AND INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated backgrounds at the ions monitored. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing field and laboratory blanks as described in Sections 9.1.1 and 9.2.2.

4.2 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, reagents are cleaned by extraction or solvent rinsing. The toxic PCB congeners 105, 114, 118, 123, 156, 157, 167, and 180 have been shown to be very difficult to completely eliminate from the laboratory, and baking of glassware in a kiln or furnace at 450-500°C may be necessary to remove these and other contaminants.

4.3 Proper cleaning of glassware is extremely important because glassware may not only contaminate the samples but may also remove the analytes of interest by adsorption onto the glass surface.

4.3.1 Glassware should be rinsed with methanol and washed with a detergent solution as soon after use as is practical. Sonication of glassware containing a detergent solution for approximately 30 seconds may aid in cleaning. Glassware with

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removable parts, particularly separatory funnels with fluoropolymer stopcocks, must be disassembled prior to detergent washing.

4.3.2   After detergent washing, glassware should be rinsed immediately: first with methanol, then with hot tap water. The tap water rinse is followed by distilled water, methanol, and then methylene chloride rinses.

4.3.3   Baking of glassware in kiln or other high temperature furnace (450-500°C) may be warranted after particularly dirty samples are encountered. However, baking should be minimized, as repeated baking of glassware may cause active sites on the glass surface that may irreversibly adsorb PCBs.

4.3.4   Immediately prior to use, the Soxhlet apparatus should be pre-extracted with methylene chloride for 3 hours to remove any possible background contamination.

4.4   The use of high purity reagents minimizes background contamination and interference problems. Purification of solvents by distillation in all-glass systems may be required.

4.5   Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences may vary considerably with the source being sampled. Toxic PCBs are often associated with other interfering chlorinated compounds which are at concentrations several orders of magnitude higher than that of the PCBs of interest. The cleanup procedures in Section 11.3 can be used to reduce many of these interferences, but unique samples may require additional cleanup approaches.

4.6   Two high resolution capillary columns, a J&W DBXLB, 60 m x 0.25 mm x 0.25 μm (J&W), and a 50 m x 0.23 mm x 0.25 μm HT-8 (SGE), are recommended for PCB analysis because both of these columns will resolve all 13 toxic PCBs. Equivalent columns that sufficiently resolve the toxic PCBs may also be used.

4.7   If other gas chromatographic conditions or other techniques are used, the analyst is required to support the data through an adequate quality assurance program.

5.0   SAFETY

5.1   The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Nevertheless, each chemical compound should be treated as a potential health hazard. Therefore, exposure to these chemicals must be reduced to the lowest possible level by whatever means available.

5.2   The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of

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material safety data sheets should also be made available to all personnel involved in the chemical analysis.

5.3   PCBs and methylene chloride have been classified as known or suspected human or mammalian carcinogens.

5.4   Unsterilized raw sewage sludge may be a human health risk because pathogens contained within the sample, e.g., salmonella, *E. coli*, hepatitis, may be aerosolized and transported to the human host via inhalation or dermal contact with mucous membranes. All sewage sludge samples should be sterilized by 4% (v/v) nitric acid that is added to the sampling bottles prior to shipment into the field for sampling (Section 8.2). In addition, sewage sludge should only be collected and stored in bottles containing vents that prevent pressure buildup, thus avoiding the possibility of the sample spraying forcefully out of the sample container when it is opened.

6.0   APPARATUS, EQUIPMENT, AND SUPPLIES

6.1   Glassware Cleaning Equipment—Laboratory sink with overhead fume hood.

6.2   Sample Preparation Equipment

   6.2.1   Laboratory fume hood of sufficient size to contain the sample preparation equipment listed below.

   6.2.2   Glove box (optional).

   6.2.3   Oven—For determining percent moisture; capable of maintaining a temperature of $110 \pm 5°C$.

   6.2.4   Desiccator.

   6.2.5   Balances

      6.2.5.1   Analytical—Capable of weighing 0.1 mg.

      6.2.5.2   Top loading—Capable of weighing 10 mg.

6.3   Extraction Apparatus

   6.3.1   Soxhlet Apparatus

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6.3.1.1 Soxhlet—50-mm ID, 200-mL capacity with 500-mL flask (Cal-Glass LG-6900, or equivalent, except substitute 500-mL round-bottom flask for 300-mL flat-bottom flask).

6.3.1.2 Thimble—43 mm × 123 mm to fit Soxhlet (Cal-Glass LG-6901-122, or equivalent).

6.3.1.3 Heating mantle—Hemispherical, to fit 500-mL round-bottom flask (Cal-Glass LG-8801-112, or equivalent).

6.3.1.4 Variable transformer—Powerstat (or equivalent), 110-volt, 10-amp.

6.3.2 Beakers—400- to 500-mL.

6.3.3 Spatulas—Stainless steel.

6.4 Filtration Apparatus

6.4.1 Pyrex glass wool—Heated in an oven at 450-500 °C for 8 hours minimum.

6.4.2 Glass funnel—125- to 250-mL.

6.4.3 Glass-fiber or quartz fiber filter paper—Whatman GF/D (or equivalent).

6.4.4 Drying column—15- to 20-mm ID Pyrex chromatographic column equipped with coarse-glass frit or glass-wool plug.

6.5 Cleanup Apparatus

6.5.1 Pipets

6.5.1.1 Disposable, Pasteur, 150-mm long × 5-mm ID (Fisher Scientific 13-678-6A, or equivalent).

6.5.1.2 Disposable, serological, 50-mL (8- to 10- mm ID).

6.5.2 Glass chromatographic columns

6.5.2.1 150-mm long × 8-mm ID, (Kontes K-420155, or equivalent) with coarse-glass frit or glass-wool plug and 250-mL reservoir.

6.5.2.2 200-mm long × 15-mm ID, with coarse-glass frit or glass-wool plug and 250-mL reservoir.

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6.6.2.1 Concentrator tubes—10-mL, graduated (Kontes K-570050-1025, or equivalent), and 1.0 mL (Kontes K-570050-1000, or equivalent) with calibration verified. Ground-glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

6.6.2.2 Evaporation flask—500-mL (Kontes K-570001-0500, or equivalent), attached to concentrator tube with springs (Kontes K-662750-0012 or equivalent).

6.6.2.3 Snyder column—Three-ball macro (Kontes K-503000-0232, or equivalent).

6.6.2.4 Boiling chips

6.6.2.4.1 Glass or silicon carbide—Approximately 10/40 mesh, extracted with methylene chloride and baked at 450°C for 1 hour minimum.

6.6.2.4.2 Fluoropolymer (optional)—Extracted with methylene chloride.

6.6.2.5 Water bath—Heated, with concentric ring cover, capable of maintaining a temperature within ±2°C, installed in a fume hood.

6.6.3 Nitrogen blowdown apparatus—Equipped with water bath controlled in the range of 30 - 60°C (N-Evap, Organomation Associates, Inc., or equivalent), installed in a fume hood.

6.6.4 TurboVap Nitrogen blowdown apparatus—Equipped with water bath controlled in the range of 30 - 60°C, and concentrator tubes (Turbotubes, or equivalent), (Turbovap II, Zymark, or equivalent).

6.6.5 Sample vials

6.6.5.1 Amber glass, 2- to 5-mL with fluoropolymer-lined screw-cap.

6.6.5.2 Glass, 0.3-mL, conical, with fluoropolymer-lined screw or crimp cap.

6.7 Gas Chromatograph—Shall have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and shall meet all of the performance specifications in Section 10.

6.7.1 GC Columns—Each of the GC columns listed below is capable of resolving the 13 toxic PCB congeners analyzed for in this method. Other GC columns may be

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used when resolution of the PCB congeners of concern from their most closely eluting leading and trailing congeners can be demonstrated.

6.7.2   Column #1—50 m long × 0.25±0.02-mm ID; 0.25-μm film HT-8 (SGE, or equivalent).

6.7.3   Column #2—60 m long x 0.25±0.02-mm ID; 0.25-μm film DBXLB (J&W, or equivalent).

6.8   High Resolution Mass Spectrometer—28- to 40-eV electron impact ionization, shall be capable of repetitively selectively monitoring 12 exact m/z's minimum at high resolution (≥10,000) during a period less than 1.5 seconds, and shall meet all of the performance specifications in Section 10.

6.9   HRGC/HRMS Interface—The high resolution mass spectrometer (HRMS) shall be interfaced to the high resolution gas chromatograph (HRGC) such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beams.

6.10   Data System—Capable of collecting, recording, and storing MS data.

7.0   REAGENTS AND STANDARDS

Note: unless otherwise stated, all reagents, water, and solvents must be pesticide grade (if available) or equivalent.

7.1   Acid and Base Partitioning

7.1.1   Potassium hydroxide—Dissolve 20 g pesticide grade (if available) KOH in 100 mL reagent water.

7.1.2   Sulfuric acid—Pesticide grade (if available; specific gravity 1.84).

7.1.3   Hydrochloric acid—Pesticide grade (if available), 6N.

7.1.4   Sodium chloride—Pesticide grade (if available), prepare at 5% (w/v) solution in reagent water.

7.2   Solution Drying and Evaporation

7.2.1   Solution drying—Sodium sulfate, reagent grade, granular, anhydrous (Baker 3375, or equivalent), rinsed with methylene chloride (20 mL/g), baked at 400°C for 1 hour minimum, cooled in a desiccator, and stored in a pre-cleaned glass

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bottle with screw-cap that prevents moisture from entering. If, after heating, the sodium sulfate develops a noticeable grayish cast (due to the presence of carbon in the crystal matrix), that batch of reagent is not suitable for use and should be discarded. Extraction with methylene chloride (as opposed to simple rinsing) and baking at a lower temperature may produce sodium sulfate that is suitable for use.

7.2.2   Prepurified nitrogen = 99.9995% purity.

7.2.3   Diatomaceous earth drying agent, Extrelut, Hydromatrix, or equivalent.

7.2.4   Desiccant—EM Science silica gel Grade H Type IV Indicating (6-16 mesh).

7.3   Extraction

7.3.1   Solvents—Acetone, n-hexane, methanol, methylene chloride, and nonane; distilled in glass, pesticide quality, lot-certified to be free of interferences.

7.4   Adsorbents for Sample Cleanup

7.4.1   Silica gel

7.4.1.1   Activated silica gel—100-200 mesh, Supelco 1-3651 (or equivalent), rinsed with methylene chloride, baked at 180°C for a minimum of 1 hour, cooled in a desiccator, and stored in a precleaned glass bottle with screw-cap that prevents moisture from entering.

7.4.1.2   Acid silica gel (30% w/w)—Thoroughly mix 44 g of concentrated sulfuric acid with 100 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a screw-capped bottle with fluoropolymer-lined cap.

7.4.1.3   Basic silica gel—Thoroughly mix 30 g of 1N sodium hydroxide with 100 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a screw-capped bottle with fluoropolymer-lined cap.

7.4.2   Carbon

7.4.2.1   Carbopak C—(Supelco 1-0258, or equivalent).

7.4.2.2   Celite 545—(Supelco 2-0199, or equivalent).

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7.4.2.3 Thoroughly mix 18 g Carbopak C and 18 g Celite 545 to produce a 50% w/w mixture. Activate the mixture at 130°C for a minimum of 6 hours. Store in a desiccator.

7.5 Copper (granular)—Copper must be used within one hour of being activated using the following procedure:

7.5.1 Add sufficient copper to process the sample set (one sample uses approximately 2 g of copper).

7.5.2 Add sufficient reagent water to the beaker so that the water level is above the copper.

7.5.3 Add an equal amount of 12N HCl to the beaker.

7.5.4 Stir mixture for approximately 30 seconds, and then discard the liquid into acid waste.

7.5.5 Rinse copper three times each with the following (listed in order): reagent water, acetone, and methylene chloride.

7.6 Standard Solutions

Standards purchased as solutions or mixtures with certification to their purity, concentration, and authenticity, or prepared from materials of known purity and composition. If the chemical purity is 98 percent or greater, the weight may be used without correction to compute the concentration of the standard. Standards should be stored in the dark in a freezer at ≤0°C in screw-capped vials with fluoropolymer-lined caps when not being used. A mark is placed on the vial at the level of the solution so that solvent loss by evaporation can be detected. If solvent loss has occurred, or the shelf life has expired, the solution should be replaced.

7.6.1 Stock Standard Solutions

7.6.1.1 Prepared in nonane per the steps below or purchase as dilute solutions (Cambridge Isotope Laboratories/CIL, Woburn, MA, or equivalent). Observe the safety precautions in Section 5.

7.6.1.2 An appropriate amount of assayed reference material is dissolved in solvent. For example, weigh 1 to 2 mg of PCB 126 to three significant figures in a 10-mL ground-glass-stoppered volumetric flask and fill to the mark with nonane. After the PCB is completely dissolved, transfer the solution to a clean 15-mL vial with fluoropolymer-lined cap.

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7.6.1.3 Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards. Reference standards that can be used to determine the accuracy of calibration standards are available from several vendors.

7.6.2 Precision and Recovery (PAR) Stock Solution

Using the solutions in Section 7.6.1, prepare the PAR stock solution to contain the PCBs of interest at the concentrations shown in Table 3. When diluted, the solution will become the PAR spiking solution (Section 7.6.7).

7.6.3 Internal Standard Solutions

7.6.3.1 Internal Standard Stock Solution

From stock standard solutions, or from purchased mixtures, prepare this solution to contain the labeled internal standards in nonane at the stock solution concentrations shown in Table 3. The solution is diluted with acetone prior to use (Section 7.6.3.2).

7.6.3.2 Internal Standard Spiking Solution

Dilute a sufficient volume of the labeled compound solution (Section 7.6.3.1) by a factor of 500 with acetone to prepare a diluted spiking solution. Concentrations may be adjusted to compensate for background levels. Each sample requires 1.0 mL of the diluted solution.

7.6.4 Cleanup Standard Spiking Solution

7.6.4.1 Prepare labeled PCBs 81 and 111 in acetone at the level shown in Table 3.

7.6.4.2 The cleanup standard is added to the sludge extract prior to cleanup to measure the efficiency of the cleanup process.

7.6.5 Recovery Standard(s) Spiking Solution

Prepare the recovery standard spiking solution to contain labeled PCBs 52, 101, 138, and 178 in nonane at the level shown in Table 3.

7.6.6 Calibration Standards (CS1 through CS5)

7.6.6.1 Combine the solutions in Sections 7.6 to produce the five calibration solutions shown in Table 4 in nonane.

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7.6.6.2 Calibration standards may also be purchased already prepared in nonane (CIL).

7.6.6.3 These solutions permit the relative response factor (labeled to native) to be measured as a function of concentration. The CS3 standard is used for calibration verification (VER).

7.6.7 Precision and Recovery (PAR) Spiking Solution

7.6.7.1 Used for preparation of laboratory spike samples (Section 9.5).

7.6.7.2 Dilute 200 µL of the PAR stock solution (Section 7.6.2) to 10 mL with acetone. 1.0 mL is required for each laboratory spike sample. Concentrations of individual PCBs may be adjusted in this solution to compensate for background levels.

7.6.8 GC Retention Time Window Defining and Isomer Specificity Test Solution

7.6.8.1 This solution is used to define the beginning and ending retention times for the PCB congeners and to demonstrate isomer specificity of the GC columns.

7.6.8.2 The solution must contain the compounds listed in Table 8 (CIL, or equivalent), at a minimum.

7.6.9 QC Check Sample

If available, a QC check sample should be obtained from a source independent of the calibration standards. Ideally, this check sample would be a certified standard reference material (SRM) containing the PCBs in known concentrations in a sample matrix similar to the matrix being analyzed.

7.6.10 HPLC Fractionation Time Standard

Prepare a solution containing both 4,4'-dibromooctafluorobiphenyl (DBOFB) and perylene at a concentration level of 20 μg/mL in methylene chloride.

7.6.11 Solution Stability

7.6.11.1 Standard solutions used for quantitative purposes (Section 7.6.6) should be analyzed periodically, and should be assayed against reference standards before further use.

7.6.11.2 If the analysis yields standard concentrations that are not within 25% of the true value for any PCB, the solutions will be replaced with solutions

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that, when analyzed, yield concentrations that are within 25% of the true value.

8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection

Sewage sludge sample bottles must be equipped with a stainless steel vent to prevent pressure buildup.

8.2 Pre-Treatment/Sterilization

Sample bottle must contain enough 1:1 HNO_3 to give 4% HNO_3 (v/v) for sterilization.

8.3 Sample Storage

Maintain semi-solid sludge samples in the dark at $\leq 4°C$ from the time of collection until receipt at the laboratory.

8.4 Holding Times

8.4.1 Samples are stored in the dark at $\leq 4°C$.

8.4.2 Sample extracts are stored in the dark at $< -10°C$ until analyzed.

8.4.3 A maximum of 30 days between sample collection and extraction, and a maximum of 45 days between extraction and analysis is recommended.

9.0 QUALITY ASSURANCE/QUALITY CONTROL

9.1 The minimum requirements of this method consist of spiking samples with labeled compounds to evaluate and document analyte recovery, and preparation and analysis of QC samples including blanks and duplicates. Laboratory performance is compared to target performance criteria to establish the performance requirements of the method.

9.2 Labeled Compounds

The laboratory shall spike all samples with the labeled standard spiking solutions (Sections 7.6.3.2 and 7.6.4) to assess method performance on the sample matrix. Recovery of labeled standards from samples should be assessed and records should be maintained.

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9.2.1 Analyze each sample according to the procedures in Section 11. Compute the percent recovery of the labeled standards as described in Section 12.2.2.

9.2.2 The recovery of each labeled compound will be compared to the target limits in Table 5. If the recovery of any compound falls outside of these limits, the data will be flagged and impact on reported concentration will be discussed in the reported results.

9.3 Laboratory Method Blanks

9.3.1 Prepare, extract, clean up, and concentrate a laboratory method blank with each sample batch (samples of the same matrix started through the extraction process on the same 12-hour shift, to a maximum of 20 samples).

9.3.2 If any native PCB analytes (Table 1) are found in the blank at greater than 20 percent of the concentration level found in the sample, the reported data should be flaggged as potentially containing some contribution from laboratory procedures. If method blank contamination is severe, sample preparation and analysis procedures should be reviewed and reprocessing the sample set should be considered depending on specific project requirements.

9.4 QC Check Sample

If available, analyze a QC check sample (Section 7.6.9) periodically to assure the accuracy of calibration standards and the overall reliability of the analytical process. It is suggested that the QC check sample be analyzed at least quarterly.

9.5 Laboratory Spike Samples

9.5.1 With each sample batch, spike duplicate sludge samples with PAR spiking solution (Section 7.6.7) and process through extraction, cleanup, and analysis procedures as the field samples.

9.5.2 Calculate precision for the duplicate laboratory spike samples as the relative percent difference (RPD). The RPD should be ≤ 50 percent.

9.5.3 Calculate accuracy for the laboratory spike samples by determining the percent of recovery of spiked analytes. Accuracy should be within 40 - 160 percent for analytes spiked five times the background level of the sludge samples.

9.6 Method Specifications

9.6.1 The specifications contained in this method can be met if the apparatus used is calibrated properly and then maintained in a calibrated state.

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9.6.2   The standards used for calibration (Section 7.6.6), calibration verification (Section 7.6.6.3), and for laboratory spike samples (Section 7.6.7) should be identical, so that the most precise results will be obtained.

9.6.3   A HRGC/HRMS instrument will provide the most reproducible results if dedicated to the settings and conditions required for the analyses of PCB analytes by this method.

10.0   HRGC/HRMS CALIBRATION

10.1   Operating Conditions

Establish the operating conditions necessary to meet the minimum retention times for the internal and recovery standards in Table 2.

10.1.1   Suggested HRGC Operating Conditions

Injector temperature:	290°C
Interface temperature:	290°C
Initial temperature:	150°C
Initial time:	2 min
Temperature program:	150 to 200°C at 10°C/min; 200 to 280°C at 2°C/min

NOTE: All portions of the column that connect the HRGC to the ion source shall remain at or above the interface temperature specified above during analysis to preclude condensation of less volatile compounds.

The HRGC conditions may be optimized for compound separation and sensitivity. Once optimized, the same HRGC conditions must be used for the analysis of all standards, blanks, and samples.

10.1.2   High Resolution Mass Spectrometer (HRMS) Resolution

10.1.2.1   Obtain a selected ion current profile (SICP) of each analyte listed in Table 3 at the two exact m/z's specified in Table 6 and at ≥10,000 resolving power by injecting an authentic standard of the PCBs either singly or as part of a mixture in which there is no interference between closely eluted components.

10.1.2.2   The analysis time for PCBs may exceed the long-term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass)

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can have serious adverse effects on instrument performance. Therefore, a mass-drift correction is mandatory and a lock-mass m/z from PFK is used for drift correction. The lock-mass m/z is dependent on the exact m/z's monitored within each descriptor, as shown in Table 6. The level of PFK metered into the HRMS during analyses should be adjusted so that the amplitude of the most intense selected lock-mass m/z signal (regardless of the descriptor number) does not exceed 10 percent of the full-scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

NOTE: Excessive PFK (or any other reference substance) may cause noise problems and contamination of the ion source necessitating increased frequency of source cleaning.

10.1.2.3   If the HRMS has the capability to monitor resolution during the analysis, it is acceptable to terminate the analysis when the resolution falls below 10,000 to save reanalysis time.

10.1.2.4   Using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 (10 percent valley) at m/z 380.9760. For each descriptor (Table 6), monitor and record the resolution and exact m/z's of three to five reference peaks covering the mass range of the descriptor. The resolution must be greater than or equal to 10,000, and the deviation between the exact m/z and the theoretical m/z (Table 6) for each exact m/z monitored must be less than 5 ppm.

10.1.3   Ion Abundance Ratios, Minimum Levels, Signal-to-Noise Ratios, and Absolute Retention Times

10.1.3.1   Choose an injection volume of either 1- or 2-μL, consistent with the capability of the HRGC/HRMS instrument. Inject a 1- or 2-μL aliquot of the CS1 calibration solution (Table 4) using the GC conditions from Section 10.1.1.

10.1.3.2   Measure the SICP areas for each analyte, and compute the ion abundance ratios at the exact m/z's specified in Table 6. Compare the computed ratio to the theoretical ratio given in Table 7.

The exact m/z's to be monitored in each descriptor are shown in Table 6. Each group or descriptor shall be monitored in succession as a function of GC retention time to ensure that all of the toxic PCBs are detected. Additional m/z's may be monitored in each

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descriptor, and the m/z's may be divided among more than the descriptors listed in Table 6, provided that the laboratory is able to monitor the m/z's of all the PCBs that may elute from the GC in a given retention-time window.

The mass spectrometer shall be operated in a mass-drift correction mode, using PFK to provide lock m/z's. The lock mass for each group of m/z's is shown in Table 6. Each lock mass shall be monitored and shall not vary by more than ±20 percent throughout its respective retention time window. Variations of the lock mass by more than 20 percent indicate the presence of coeluting interferences that may significantly reduce the sensitivity of the mass spectrometer. Reinjection of another aliquot of the sample extract will not resolve the problem. Additional cleanup of the extract may be required to remove the interferences.

10.1.3.3   All PCB analytes and labeled compounds in the CS1 standard shall be within the QC limits in Table 7 for their respective ion abundance ratios; otherwise, the mass spectrometer shall be adjusted and this test repeated until the m/z ratios fall within the limits specified. If the adjustment alters the resolution of the mass spectrometer, resolution shall be verified (Section 10.1.2) prior to repeat of the test.

10.1.3.4   The peaks representing the PCBs and labeled compounds in the CS1 calibration standard must have signal-to-noise ratios (S/N) greater than or equal to 10.0. Otherwise, the mass spectrometer shall be adjusted and this test repeated until the peaks have signal-to-noise ratios (S/N) greater than or equal to 10.0.

10.1.3.5   Retention Time Windows—Analyze the GC retention time window defining and isomer specificity test solution (Section 7.6.8) using the optimized temperature program in Section 10.1.1. Table 2 gives the elution order (first/last) of the window-defining compounds.

10.1.4   Isomer Specificity

10.1.4.1   From the analysis of the GC retention time window and isomer specificity test solution (Section 10.1.3.5), compute the percent valley between the GC peaks for PCB 123 and PCB 118, and between the GC peaks for PCB 156 and 157.

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10.1.4.2 Verify that the height of the valley between these closely eluted isomers and the PCBs given in Section 10.1.4.1 is less than 25 percent. If the valley exceeds 25 percent, adjust the analytical conditions and repeat the test or replace the GC column and recalibrate.

10.2 Initial Calibration

10.2.1 Prepare a calibration curve encompassing the concentration range for each compound to be determined. Referring to Table 2, calculate the relative response factors for unlabeled target analytes (RF_n) relative to their appropriate internal standard (Table 3) and the relative response factors for the $^{13}C_{12}$-labeled internal standards (RF_{is}) using the four recovery standards (Table 3) according to the following formulae:

$$RF_n = \frac{(A_n^1 + A_n^2) \times Q_{is}}{(A_{is}^1 + A_{is}^2) \times Q_n}$$

$$RF_{is} = \frac{(A_{is}^1 + A_{is}^2) \times Q_{rs}}{(A_{rs}^1 + A_{rs}^2) \times Q_{is}}$$

where:

A_n^1 *and* A_n^2 = *sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and 6) for unlabeled PCBs,*

A_{is}^1 *and* A_{is}^2 = *sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and 6) for the labeled internal standards,*

A_{rs}^1 *and* A_{rs}^2 = *sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and 6) for the recovery standard,*

Q_{is} = *quantity of the internal standard injected (pg),*

Q_{rs} = *quantity of the recovery standard injected (pg), and*

Q_n = *quantity of the unlabeled PCB analyte injected (pg).*

RF_n and the RF_{is} are dimensionless quantities; the units used to express Q_{is}, Q_{rs}, and Q_n must be the same.

10.2.2 Calculate the mean relative response factor values and their respective percent relative standard deviation (%RSD) for the five calibration solutions. If the mean relative response factors between the analytes is not within 35% RSD, the instrument must be re-calibrated.

$$\overline{RF_n} = \frac{\displaystyle\sum_{j=1}^{5} RF_{n(j)}}{5}$$

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where n represents a particular PCB congener (n = 1 to 13; Table 3), and j is the injection or calibration solution number; (j = 1 to 5).

$$\overline{RF_{is}} = \frac{\sum_{j=1}^{5} RF_{is(j)}}{5}$$

where is represents a particular PCB internal standard (is = 14 to 23; Table 3), and j is the injection or calibration solution number; (j = 1 to 5).

10.3 Operation Verification

At the beginning of each 12-hour shift during which analyses are performed, HRGC/HRMS system performance and calibration are verified for all native PCBs and labeled compounds. For these tests, analysis of the CS3 calibration verification (VER) standard (Section 7.6.6 and Table 4) and the isomer specificity test solution (Section 7.6.8 and Table 8) shall be used to verify all performance criteria. Adjustment and/or recalibration (Section 10) shall be performed until all performance criteria are met. Only after all performance criteria are met may samples and blanks be analyzed.

10.3.1 HRMS Resolution

A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at the appropriate m/z before any analysis is performed. Static resolving power checks must be performed at the beginning and at the end of each analysis batch according to procedures in Section 10.1.2. Corrective actions must be implemented whenever the resolving power does not meet the requirement.

10.3.2 Calibration Verification

10.3.2.1 Inject the VER standard using the procedure in Section 11.12.3.

10.3.2.2 The m/z abundance ratios for all PCBs shall be within the limits in Table 7; otherwise, the mass spectrometer shall be adjusted until the m/z abundance ratios fall within the limits specified, and the verification test shall be repeated. If the adjustment alters the resolution of the mass spectrometer, resolution shall be verified (Section 10.1.2) prior to repeat of the verification test.

10.3.2.3 The peaks representing each native PCB and labeled compound in the VER standard must be present with a S/N of at least 10; otherwise, the mass spectrometer shall be adjusted and the verification test repeated.

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10.3.2.4 Calculate the relative response factors (RF) for unlabeled target analytes [$RF_{(n)}$; n = 1 to 13 from Table 3] relative to their appropriate internal standards (Table 2), and the RF_{is} for the $^{13}C_{12}$-labeled internal standards [$RF_{(is)}$; is = 14-23] relative to the recovery standards (Table 2) using the equations shown in Section 10.2.1.

10.3.2.5 For each compound, compare the relative response factor with those generated in the initial calibration. Relative response factors should be within 35 percent of initial calibration results for 70% of the analytes for the calibration to be verified. Once verified, analysis of standards and sample extracts may proceed. If, however, fewer than 70% of the response factors are within the 35% limit, the measurement system is not performing properly for those compounds. In this event, prepare a fresh calibration standard or correct the problem causing the failure and repeat the resolution (Section 10.3.1) and calibration verification (Section 10.3.2) tests, or recalibrate (Section 10). Per the analyst's discretion, results may also be reported for these analytes using the average calibration verification response factors bracketing the samples rather than the mean response factor generated in the initial calibration. If this option is chosen, data reported using an average calibration verification response factor should be flagged and discussed in the final report.

10.3.3 Retention Times

The absolute retention times of the GC/MS internal standards in the calibration verification shall be within ±15 seconds of the retention times obtained during initial calibration.

10.3.4 HRGC Resolution

10.3.4.1 Inject the GC retention time window defining and isomer specificity test solution (Section 7.6.8).

10.3.4.2 The valley height between PCBs 123 and 118 at m/z 325.8804 shall not exceed 25 percent, and the valley height between PCBs 156 and 157 shall not exceed 25 percent at m/z 359.8415 on the GC columns.

10.3.4.3 If the absolute retention time of any compound is not within the limits specified or if the congeners are not resolved, the GC is not performing properly. In this event, adjust the GC and repeat the calibration verification test or recalibrate, or replace the GC column and either verify calibration or recalibrate.

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where n represents a particular PCB congener (n = 1 to 13; Table 3), and j is the injection or calibration solution number; (j = 1 to 5).

$$\overline{RF_{is}} = \frac{\sum\limits_{j=1}^{5} RF_{is(j)}}{5}$$

where is represents a particular PCB internal standard (is = 14 to 23; Table 3), and j is the injection or calibration solution number; (j = 1 to 5).

10.3   Operation Verification

At the beginning of each 12-hour shift during which analyses are performed, HRGC/HRMS system performance and calibration are verified for all native PCBs and labeled compounds. For these tests, analysis of the CS3 calibration verification (VER) standard (Section 7.6.6 and Table 4) and the isomer specificity test solution (Section 7.6.8 and Table 8) shall be used to verify all performance criteria. Adjustment and/or recalibration (Section 10) shall be performed until all performance criteria are met. Only after all performance criteria are met may samples and blanks be analyzed.

10.3.1   HRMS Resolution

A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at the appropriate m/z before any analysis is performed. Static resolving power checks must be performed at the beginning and at the end of each analysis batch according to procedures in Section 10.1.2. Corrective actions must be implemented whenever the resolving power does not meet the requirement.

10.3.2   Calibration Verification

10.3.2.1   Inject the VER standard using the procedure in Section 11.12.3.

10.3.2.2   The m/z abundance ratios for all PCBs shall be within the limits in Table 7; otherwise, the mass spectrometer shall be adjusted until the m/z abundance ratios fall within the limits specified, and the verification test shall be repeated. If the adjustment alters the resolution of the mass spectrometer, resolution shall be verified (Section 10.1.2) prior to repeat of the verification test.

10.3.2.3   The peaks representing each native PCB and labeled compound in the VER standard must be present with a S/N of at least 10; otherwise, the mass spectrometer shall be adjusted and the verification test repeated.

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10.3.2.4 Calculate the relative response factors (RF) for unlabeled target analytes [$RF_{(n)}$; n = 1 to 13 from Table 3] relative to their appropriate internal standards (Table 2), and the RF_{is} for the $^{13}C_{12}$-labeled internal standards [$RF_{(is)}$; is = 14-23] relative to the recovery standards (Table 2) using the equations shown in Section 10.2.1.

10.3.2.5 For each compound, compare the relative response factor with those generated in the initial calibration. Relative response factors should be within 35 percent of initial calibration results for 70% of the analytes for the calibration to be verified. Once verified, analysis of standards and sample extracts may proceed. If, however, fewer than 70% of the response factors are within the 35% limit, the measurement system is not performing properly for those compounds. In this event, prepare a fresh calibration standard or correct the problem causing the failure and repeat the resolution (Section 10.3.1) and calibration verification (Section 10.3.2) tests, or recalibrate (Section 10). Per the analyst's discretion, results may also be reported for these analytes using the average calibration verification response factors bracketing the samples rather than the mean response factor generated in the initial calibration. If this option is chosen, data reported using an average calibration verification response factor should be flagged and discussed in the final report.

10.3.3 Retention Times

The absolute retention times of the GC/MS internal standards in the calibration verification shall be within ±15 seconds of the retention times obtained during initial calibration.

10.3.4 HRGC Resolution

10.3.4.1 Inject the GC retention time window defining and isomer specificity test solution (Section 7.6.8).

10.3.4.2 The valley height between PCBs 123 and 118 at m/z 325.8804 shall not exceed 25 percent, and the valley height between PCBs 156 and 157 shall not exceed 25 percent at m/z 359.8415 on the GC columns.

10.3.4.3 If the absolute retention time of any compound is not within the limits specified or if the congeners are not resolved, the GC is not performing properly. In this event, adjust the GC and repeat the calibration verification test or recalibrate, or replace the GC column and either verify calibration or recalibrate.

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10.4   Data Storage

MS data shall be collected, recorded, and stored.

10.4.1   Data Acquisition

The signal at each exact m/z shall be collected repetitively throughout the
monitoring period and stored on a mass storage device.

10.4.2   Response Factors and Multipoint Calibrations

The data system shall be used to record and maintain lists of response factors
and multipoint calibration curves. Computations of relative standard deviation
(coefficient of variation) shall be used to test calibration linearity.

11.0 PROCEDURE

11.1   Sample preparation involves mixing the wet sludge sample with a drying agent so that the
toxic PCBs can be extracted efficiently. For samples known or expected to contain high
levels of the PCBs, the smallest sample size representative of the entire sample should be
used. With each sample set, a laboratory method blank and duplicate laboratory spike
samples must be processed through the same steps as the sample to check for
contamination and losses in the preparation processes. Percent moisture is determined
using the procedures in Section 11.2, and a 2 g sample aliquot (wet weight) is extracted as
described in Section 11.3.

11.2   Percent Moisture Determination

Note: This aliquot is used for determining the moisture content of sewage sludge
samples and not for determination of PCBs.

11.2.1   Weigh or tare a weighing pan or beaker to three significant figures

11.2.2   Transfer 10.0 ± 0.02 g of well-mixed sample to the pan or beaker

11.2.3   Weigh and record the wet sample plus beaker

11.2.4   Dry the sample for a minimum of 12 hours at $110 \pm 5°C$ and cool in a
desiccator until the sample has equilibrated to room temperature. Weigh the dry
sample plus beaker.

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11.2.5   Calculate percent moisture as follows:

$$\% \ moisture = \frac{W_{before} - W_{after}}{10 \ g} \times 100$$

where: _

W_{before} =   *weight of sample plus beaker before drying (g),*
W_{after} =   *weight of sample plus beaker after drying (g),*

11.3   Preparation of Sewage Sludge Samples

11.3.1   Weigh a well-mixed 2.0 g aliquot of the wet sludge sample into a clean beaker or glass jar.

11.3.2   Spike the diluted labeled internal standard solution (Section 7.6.3.2) into the sample.

11.3.3   For each sample or sample batch (to a maximum of 20 samples) to be extracted during the same 12 hour shift, prepare a laboratory method blank by spiking the internal standard solution into an empty, clean beaker or glass jar.

11.3.4   If a laboratory spike sample is being prepared, add 1 mL of the PAR spiking solution at this time.

11.3.5   Stir or tumble, and then equilibrate the aliquots for 1 to 2 hours.

11.3.6   Homogenize the sample into a slurry using a glass rod.

11.3.7   Mix the slurry with sufficient drying agent (Section 7.2.3) to provide a 1:1 ratio (2 g), and extract the mixture using the Soxhlet procedure described in Section 11.4.1.

11.4   Extraction and Concentration

The sewage sludge sample is extracted using the Soxhlet technique. Macro-concentration procedures include rotary evaporation, Turbovap, and Kuderna-Danish (K-D) evaporation. Micro-concentration uses nitrogen blowdown.

11.4.1   Soxhlet Extraction

11.4.1.1   Place a clean extraction thimble (Section 6.3.1.2) in a clean extractor.

11.4.1.2 Place 30 to 40 mL of methylene chloride in the receiver and 200 to 250 mL of methylene chloride in the flask.

11.4.1.3 Load the sample mixture into the thimble. For laboratory method blanks and spikes, rinse the contents of the beaker or glass jar four times with methylene chloride. Add the rinses to the extractor.

11.4.1.4 Reassemble the Soxhlet apparatus, and apply power to the heating mantle to begin extracting. Frequently check the apparatus for foaming during the first 2 hours of extraction. If foaming occurs, reduce the extraction rate until foaming subsides.

11.4.1.5 Extract the sample for a total of 16 to 24 hours. Cool and disassemble the apparatus.

11.4.1.6 Concentrate the extract to approximately 10 mL; split the sample extract into two equal portions (5 mL each). Transfer 5 mL of the extract to a glass storage vial with a PTFE lined cap. Label the extract, mark the liquid level on the vial with a permanent marker to monitor solvent evaporation during storage, and store at 0°C.

11.4.1.7 Solvent exchange the other half of the extract (5 mL) into hexane by adding 10 mL of hexane, concentrating down to 1 mL using K-D evaporation, adding 10 mL hexane, and concentrating down again to 2 mL. Transfer the extract with three aliquots (15 mL each) of hexane into a 250-mL separatory funnel. Proceed to Section 11.5 to start cleanup procedures.

11.5   Acid and Base Partitioning

11.5.1 Spike 1.0 mL of the cleanup standard (Section 7.6.4) into the separatory funnels containing the sample, laboratory method blank, and duplicate laboratory spike sample extracts from Section 11.3.

11.5.2 Partition the extract against 50 mL of sulfuric acid (Section 7.1.2). Shake for 2 minutes with periodic venting into a hood. Remove and discard the aqueous layer. Repeat the acid washing until no color is visible in the aqueous layer to a maximum of four washings.

11.5.3 Partition the extract against 50 mL of sodium chloride solution (Section 7.1.4) in the same way as with the acid. Discard the aqueous layer.

11.5.4 Partition the extract against 50 mL of potassium hydroxide solution (Section 7.1.1) in the same way as with the acid. Repeat the base washing until no color is visible in the aqueous layer to a maximum of four washings. Minimize

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contact time between the extract and the base to prevent degradation of the PCBs.

11.5.5 Repeat the partitioning against sodium chloride solution two more times. each time discarding the aqueous layer.

11.5.6 Pour each extract through a drying column containing 7 to 10 cm of granular anhydrous sodium sulfate (Section 7.2.1). Rinse the separatory funnel with 30 to 50 mL of solvent, and pour through the drying column. Collect each extract in a round-bottom flask.

11.5.7 Concentrate the extract to 1 mL using either rotovap, K-D concentration, or Turbovap (Section 11.6). After concentration, proceed to Section 11.7 for sulfur cleanup.

11.6 Macro-Concentration—Extracts in methylene chloride or n-hexane are concentrated using rotary evaporation, a Kuderna-Danish, or Turbovap apparatus.

11.6.1 Rotary evaporation—Concentrate the extracts in separate round-bottom flasks.

Note: Improper use of the rotary evaporator may cause contamination of the sample extract.

11.6.1.1 Assemble the rotary evaporator according to manufacturer's instructions, and warm the water bath to 45 °C. On a daily basis, preclean the rotary evaporator by concentrating 100 mL of clean extraction solvent through the system. Archive both the concentrated solvent and the solvent in the catch flask for a contamination check if necessary. Between samples, use three 2- to 3-mL aliquots of solvent to rinse the feed tube between samples. Collect waste in a waste beaker.

11.6.1.2 Attach the round-bottom flask containing the sample extract to the rotary evaporator. Slowly apply vacuum to the system, and begin rotating the sample flask.

11.6.1.3 Lower the flask into the water bath, and adjust the speed of rotation and the temperature as required to complete concentration in 15 to 20 minutes. At the proper rate of concentration, the flow of solvent into the receiving flask must be steady, with no bumping or visible boiling of the extract occurring.

Note: If the rate of concentration is too fast, analyte loss may occur.

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11.6.1.4 When the liquid in the concentration flask has reached an apparent volume of approximately 2 mL, remove the flask from the water bath and stop the rotation. Slowly and carefully admit air into the system. Be sure not to open the valve so quickly that the sample is blown out of the flask. Rinse the feed tube with approximately 2 mL of solvent.

11.6.2 Kuderna-Danish (K-D)—Concentrate the extracts in separate 500-mL K-D flasks equipped with 10-mL concentrator tubes. The K-D technique is used for solvents such as methylene chloride and n-hexane.

11.6.2.1 Add 1 to 2 clean boiling chips to the receiver. Attach a three-ball macro-Snyder column. Pre-wet the column by adding approximately 1 mL of solvent through the top. Place the K-D apparatus in a hot water bath so that the entire lower rounded surface of the flask is bathed with steam.

11.6.2.2 Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

11.6.2.3 When the liquid has reached an apparent volume of 1 mL, remove the K-D apparatus from the bath and allow the solvent to drain and cool for at least 10 minutes.

11.6.2.4 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of solvent. A 5-mL syringe is recommended for this operation.

11.6.2.5 Remove the three-ball Snyder column, add a fresh boiling chip, and attach a two-ball micro-Snyder column to the concentrator tube. Pre-wet the column by adding approximately 0.5 mL of solvent through the top. Place the apparatus in the hot water bath.

11.6.2.6 Adjust the vertical position and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

11.6.2.7 When the liquid reaches an apparent volume of 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes.

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11.6.3　Turbovap —Concentrate the extracts in separate 250-mL Turbotubes. The Turbovap technique is used for solvents such as methylene chloride and n-hexane.

11.7　Sulfur Cleanup

11.7.1　Add approximately 2 g of clean copper (Section 7.5) to a centrifuge tube.

11.7.2　Vigorously mix the extract and the copper powder for at least 1 minute.

11.7.3　Allow the extract to react with the copper powder for 1 hour.

11.7.4　Separate the extract from the copper by drawing off the extract with a disposable pipet and transfer to a clean concentrator vial. Rinse the copper powder with three additional 5-mL aliquots of n-hexane and add rinses to the vial.

11.7.5　The extract is concentrated to 1 mL. Proceed to Section 11.8 for silica gel cleanup.

11.8　Silica Gel Cleanup

11.8.1　Place a glass-wool plug in a 15-mm ID chromatography column (Section 6.5.2.2). Pack the column bottom to top with 1 g silica gel (Section 7.4.1.1), 4 g basic silica gel (Section 7.4.1.3), 1 g silica gel, 8 g acid silica gel (Section 7.4.1.2), 2 g silica gel, and 4 g granular anhydrous sodium sulfate (Section 7.2.1). Tap the column to settle the adsorbents.

11.8.2　Pre-elute the column with 50 to 100 mL of n-hexane. Close the stopcock when the n-hexane is within 1 mm of the sodium sulfate. Discard the eluate. Check the column for channeling. If channeling is present, discard the column and prepare another.

11.8.3　Apply the concentrated extract to the column. Open the stopcock until the extract is within 1 mm of the sodium sulfate.

11.8.4　Rinse the receiver twice with 1-mL portions of n-hexane, and apply separately to the column. Elute the PCBs with 75 mL of n-hexane and collect the eluate.

11.8.5　Concentrate the eluate per Section 11.6 and proceed to Section 11.9 for carbon column cleanup.

11.8.6　For extracts of samples known to contain large quantities of other organic compounds, it may be advisable to increase the capacity of the silica gel column. This may be accomplished by increasing the strengths of the acid and basic silica gels. The acid silica gel (Section 7.4.1.2) may be increased in

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strength to as much as 44% w/w (7.9 g sulfuric acid added to 10 g silica gel). The basic silica gel (Section 7.4.1.3) may be increased in strength to as much as 33% w/w (50 mL 1N NaOH added to 100 g silica gel). Additional acid silica (only) columns may be used until the extract has no appearance of color.

11.9   Carbon Column Cleanup

11.9.1   Cut both ends from a 50-mL disposable serological pipet (Section 6.5.1.2) to produce a 20-cm column. Fire-polish both ends and flare both ends if desired. Insert a glass-wool plug at one end, and pack the column with 3.6 g of Cartopak/Celite (Section 7.4.2.3) to form an adsorbent bed 20 cm long. Insert a glass-wool plug on top of the bed to hold the adsorbent in place.

11.9.2   Pre-elute the column with 20 mL each in succession of methylene chloride, and n-hexane.

11.9.3   When the solvent is within 1 mm of the column packing, apply the n-hexane sample extract to the column. Rinse the sample container twice with 1-mL portions of n-hexane and apply separately to the column. Apply 2 mL of n-hexane to complete the transfer.

11.9.4   Elute the column with 25 mL of n-hexane and collect the eluate. This fraction will contain the mono- and di-ortho PCBs.

11.9.5   Elute the column with 15 mL of methanol and archive the eluate. This fraction will contain residual lipids and other potential interferents, if present.

11.9.6   Elute the column with 15 mL of toluene and collect the eluate. This fraction will contain PCBs 77, 126, and 169.

11.9.7   Combine the first and third fractions. If carbon particles are present in the combined eluate, filter through glass-fiber filter paper.

11.9.8   Concentrate the combined elute to 1 mL using rotary evaporation, K-D, or Turbovap (Section 11.6).

11.9.9   Proceed to Section 11.10 for HPLC/GPC cleanup.

11.10   High Performance Liquid Chromatography (HPLC)/Gel Permeation Chromatography (GPC)

11.10.1   GPC columns

Purchased pre-packed (see Section 6.5.3.7).

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11.10.2 HPLC fractionation time determination

    11.10.2.1   Analyze the HPLC fractionation time standard (Section 7.6.10) at least twice. If the RT differences between runs is greater than 0.1 min, reanalyze until acceptable RTs are obtained from two consecutive runs.

    11.10.2.2   Set the collection window to allow for the collection of solvent between 0.5 minutes after the elution time of DBOFB to 0.5 minutes after the elution time of perylene (Section 7.7).

    11.10.2.3   The collection window should allow for the inclusion of PCBs from the extract, while eliminating contaminants such as lipids and sulfur.

    11.10.2.4   Verify the calibration every 10 to 12 samples.

11.10.3 Extract cleanup

    11.10.3.1   Filter the extract to remove any particulates.

    11.10.3.2   Load the extract onto the autosampler and inject 600 μL onto the HPLC.

    11.10.3.3   Elute the extract using the calibration data determined in Section 11.10.2.

    11.10.3.4   Collect the eluate in a clean 60 mL fraction collector vial/tube. If a particularly dirty extract is encountered, a methylene chloride blank shall be run through the system to check for carry-over.

    11.10.3.5   Proceed to Section 11.11 for concentration to final volume.

11.11 Concentration to Final Volume

    11.11.1   The extract is concentrated in a calibrated concentrator tube to a final volume of 20 μL to 1 mL, per the analyst's discretion, under a gentle stream of nitrogen. A final extract volume of 150 μL is recommended based on the limited method demonstration.

    11.11.2   Add 15 μL of the recovery standard spiking solution (Section 7.6.5) to the sample extract.

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11.12 HRGC/HRMS Analysis

11.12.1 Establish the operating conditions given in Section 10.1, perform initial calibration if necessary (Section 10.2), or verify calibration (Section 10.3).

11.12.2 If an extract is to be reanalyzed and evaporation has occurred, do not add more recovery standard solution. Instead, bring the extract back to its previous volume (e.g., 19 μL, or 18 μL if 2 μL injections are used) with pure nonane.

11.12.3 Inject 1.0 or 2.0 μL of the concentrated extract containing the recovery standard solution, using on-column or splitless injection. The volume injected must be identical to the volume used for calibration (Section 10.1.3.1).

11.12.4 Start the HRGC column initial isothermal hold upon injection. Start HRMS data collection after the solvent peak elutes. Stop the data collection after the $^{13}C_{12}$-PCB 209 has eluted. Return the column to the initial temperature for analysis of the next extract or standard.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Qualitative Determination

A PCB analyte or labeled compound is identified in a standard, blank, or sample when all of the criteria in Sections 12.1.1 through 12.1.4 are met. If the criteria for identification in Sections 12.1.1-12.1.4 are not met, the PCB analyte has not been positively identified. If interferences preclude identification, an estimated maximum possible concentration (EMPC) can be reported (Section 12.2.6), or a new aliquot of sample may be extracted, further cleaned up, and analyzed.

12.1.1 The signals for the two exact m/z's in Table 6 must be present and must maximize within the same two seconds.

12.1.2 The signal-to-noise ratio (S/N) for the GC peak at each exact m/z must be greater than or equal to 2.5 for each PCB detected in a sample extract, and greater than or equal to 10 for all PCBs in the calibration standard (Section 7.6.6).

12.1.3 The ratio of the integrated areas of the two exact m/z's specified in Table 6 must be within the limit in Table 7, or within ±10 percent of the ratio in the midpoint (CS3) calibration or calibration verification (VER), whichever is most recent.

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12.1.4 The relative retention time of the peak for a toxic PCB must be within ±15 seconds of the retention times obtained during calibration.

12.2 Quantitative Determination

12.2.1 For gas chromatographic peaks that have met the criteria outlined in Section 12.1, calculate the concentration of the PCB compounds in the extract, using the formula:

$$C_x = \frac{A_x \times Q_{is}}{A_{is} \times \overline{RF}_n \times W_s}$$

where:

C_x = *concentration of unlabeled PCB congeners in the sample (pg/g, dry weight),*

A_x = *sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and 6) for unlabeled PCBs,*

A_{is} = *sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and 6) for the labeled internal standards,*

Q_{is} = *quantity, in pg, of the internal standard added to the sample before extraction,*

$\overline{RF}_n$ = *calculated mean relative response factor for the analyte (RF_n with n=1 to 13; Section 10.2.1),*

W_s = *weight of sample extracted (g, dry weight),*

12.2.2 Calculate the percent recovery of the internal standards measured in the sample extract, using the formula:

$$Percent\ recovery = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs} \times \overline{RF}_{is}} \times 100$$

where:

A_{is} = *sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and 6) for the labeled internal standard,*

A_{rs} = *sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and 6) for the labeled recovery standard,*

Q_{is} = *quantity, in ng, of the internal standard added to the sample before extraction,*

Q_{rs} = *quantity, in ng, of the recovery standard added to the cleaned sample extract before HRGC/HRMS analysis, and*

$\overline{RF}_{is}$ = *calculated mean relative response factor for the labeled internal standard relative to the appropriate recovery standard. This represents the mean obtained in Section 10.2.2 ($\overline{RF}_{is}$ with is = 14 to 23, Table 3).*

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The percent recovery of the cleanup standards is calculated similarly. The percent recovery should meet the criteria shown in Table 5. If recoveries are outside the limits of Table 5, the data should be flagged and the impact on reported results discussed in the final report.

12.2.3 Outside Calibration Range

12.2.3.1 If the SICP area at either quantitation m/z for any compound exceeds the calibration range of the system, the extract must be diluted and re-analyzed.

12.2.3.2 Dilute the sample extract by a factor of 10, adjust the concentration of the recovery standard to 100 pg/μL in the extract, and analyze an aliquot of this diluted extract.

12.2.4 Estimated Detection Limit (EDL)

$$EDL\ (pg\ /\ g) = \frac{2.5\ (H1_S + H2_S)\ (Q_{is})}{(H1_{is} + H2_{is})\ (RF_n)\ (W_s)}$$

where:

$H1_s$ and $H2_s$ = *The heights of the noise where the primary and secondary m/z's for the PCBs would elute.*

$H1_{is}$ and $H2_{is}$ = *The heights of the response of the primary and secondary m/z's for the internal standard,*

And Q_{is}, $\overline{RF}_n$, and W_s are as described in Section 12.2.1.

12.2.5 Estimated Maximum Possible Concentration (EMPC)

When the response of a signal having the same retention time as a toxic PCB congener has a S/N in excess of 2.5 and does not meet all of the other qualitative identification criteria listed in Section 12.1 calculate an Estimated Maximum Possible Concentration (EMPC). The EMPC is calculated using the equation in Section 12.2.1, except that A_x should represent the sum of the area under the smaller peak and of the other peak area calculated using the theoretical chlorine isotope ratio. The value shall be noted as EMPC and the results reported.

12.2.6 Results are reported to three significant figures for the PCBs and labeled compounds found in all standards, blanks, and samples.

Note: Reported results will not be adjusted for field or laboratory blank levels.

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12.2.6.1　Sewage Sludge—Report results in pg/g based on the dry weight of the sample.

12.2.6.2　Blanks—Report results above the EDL. Do not blank-correct results. If a blank accompanying a sample result shows contamination above the EDL for the congener, flag the sample result and report the results for the sample and the accompanying blank.

12.2.6.3　Dilutions (Section 12.2.3.2)

Results for PCB analytes in samples that have been diluted; for this EPA project, both the undiluted and diluted PCB results are to be reported, whether or not all of the analytes are within the calibration range.

12.2.6.4　Non-Detects

Note the non-detected PCB analytes as ND and report the estimated detection limit established during the analysis

13.0　METHOD PERFORMANCE

13.1　In a limited single laboratory demonstration of this method for sewage sludge samples, estimated detection limits of approximately 40 pg/g were achieved for pentachlorinated biphenyl (PeCB); 65 pg/g for hexachlorinated biphenyl (HxCB); and 55 pg/g for heptachlorinated biphenyl (HpCB).

13.2　Interlaboratory testing of this method to determine overall precision and bias has not been performed.

14.0　POLLUTION PREVENTION

None.

15.0　WASTE MANAGEMENT

PCB waste should be disposed of according to Toxic Substances Control Act (TSCA) guidelines 40CFR 700-789, and hazardous waste should be disposed of according to Resource Conservation and Recovery Act (RCRA) guidelines 40CFR 260-269.

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16.0 REFERENCES

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17.0   TABLES AND FIGURES

Table 1. Toxic Polychlorinated Biphenyls Determined by High Resolution Gas Chromatography (HRGC)/High Resolution Mass Spectrometry (HRMS)

PCB[1]	Native compound CAS Registry No.	IUPAC No.[2]
Target Analytes		
3,3',4,4'-TCB	32598-13-3	77
2,3,3',4,4'-PeCB	32598-14-4	105
2,3,4,4',5-PeCB	74472-37-0	114
2,3',4,4',5-PeCB	31508-00-6	118
2',3,4,4',5-PeCB	65510-44-3	123
3,3',4,4',5-PeCB	57465-28-8	126
2,3,3',4,4',5-HxCB	38380-08-4	156
2,3,3',4,4',5'-HxCB	69782-90-7	157
2,3',4,4',5,5'-HxCB	52663-72-6	167
3,3',4,4',5,5'-HxCB	32774-16-6	169
2,2',3,3',4,4',5-HpCB	35065-30-6	170
2,2',3,4,4',5,5'-HpCB	35065-29-3	180
2,3,3',4,4',5,5'-HpCB	39635-31-9	189
Internal Standards		
3,3',4,4'-TCB	160901-67-7	77L
2,3,3',4,4'-PeCB	160901-70-2	105L
2,3,4,4',5-PeCB	160901-72-4	114L
2,3',4,4',5-PeCB	160901-73-5	118L
2',3,4,4',5-PeCB	160901-74-6	123L
3,3',4,4',5-PeCB	160901-75-7	126L
2,3,3',4,4',5-HxCB	160901-77-9	156L
2,3,3',4,4',5'-HxCB	160901-78-0	157L
2,3',4,4',5,5'-HxCB	161627-18-5	167L
3,3',4,4',5,5'-HxCB	160901-79-1	169L
2,2',3,3',4,4',5-HpCB	160901-80-4	170L
2,2',3,4,4',5,5'-HpCB	160901-82-6	180L
2,3,3',4,4',5,5'-HpCB	160901-83-7	189L
Cleanup Standards		
$^{13}C_{12}$-3,4,4',5-TCB	160901-68-8	81
$^{13}C_{12}$-2,3,3',5,5'-PeCB	160901-71-3	111
Recovery Standards		
$^{13}C_{12}$-2,2',5,5'-TCB	160901-66-6	52
$^{13}C_{12}$-2,2',4,4,5'-PeCB	160901-69-9	101
$^{13}C_{12}$-2,2',3,4,4',5'-HxCB	160901-76-8	138
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB	160901-81-5	178
Final Eluter Standard		
$^{13}C_{12}$-DCB	160901-84-8	209

[1] Polychlorinated biphenyls:

   TCB = Tetrachlorobiphenyl
   PeCB = Pentachlorobiphenyl
   HxCB = Hexachlorobiphenyl
   HpCB = Heptachlorobiphenyl
   DCB = Decachlorobiphenyl

[2] Suffix "L" designates a labeled compound.

Table 2. Retention Time (RT) References, Quantitation References, and Retention Times (RTs) for the Toxic PCBs

IUPAC No.[1]	PCB congener	IUPAC No.[1]	Retention time and quantitation reference	RT[2] (min)
52L	13C12-2,2',5,5'-TCB	—[3]	13C12-2,2',5,5'-TCB	28.66
81L	13C12-3,4,4',5-TCB[4]	52L	13C12-2,2',5,5'-TCB	37.89
77L	13C12-3,3',4,4'-TCB	52L	13C12-2,2',5,5'-TCB	38.85
77	3,3',4,4'-TCB	77L	13C12-3,3',4,4'-TCB	38.85
101L	13C12-2,2',4,5,5'-PeCB	—	13C12-2,2',4,5,5'-PeCB	35.02
111L	13C12-2,3,3',5,5'-PeCB[4]	101L	13C12-2,2',4,5,5'-PeCB	37.13
123	2',3,4,4',5-PeCB	118L	13C12-2,3',4,4',5-PeCB	39.90
118L	13C12-2,3',4,4',5-PeCB	101L	13C12-2,2',4,5,5'-PeCB	40.17
118	2,3',4,4',5-PeCB	118L	13C12-2,3',4,4',5-PeCB	40.17
114	2,3,4,4',5-PeCB	105L	13C12-2,3,3',4,4'-PeCB	40.79
105L	13C12-2,3,3',4,4'-PeCB	101L	13C12-2,2',4,5,5'-PeCB	42.22
105	2,3,3',4,4'-PeCB	105L	13C12-2,3,3',4,4'-PeCB	42.22
126L	13C12-3,3',4,4',5-PeCB	101L	13C12-2,2',4,5,5'-PeCB	44.75
126	3,3',4,4',5-PeCB	126L	13C12-3,3',4,4',5-PeCB	44.75
138L	13C12-2,2',3,4,4',5'-HxCB	—	13C12-2,2',4,5,5'-PeCB	43.23
167L	13C12-2,3',4,4',5,5'-HxCB	138L	13C12-2,2',3,4,4',5'-HxCB	45.72
167	2,3',4,4',5,5'-HxCB	167L	13C12-2,3',4,4',5,5'-HxCB	45.72
156L	13C12-2,3,3',4,4',5-HxCB	138L	13C12-2,2',3,4,4',5'-HxCB	47.37
157L	13C12-2,3,3',4,4',5'-HxCB	138L	13C12-2,2',3,4,4',5'-HxCB	47.79
156	2,3,3',4,4',5-HxCB	156L	13C12-2,3,3',4,4',5-HxCB	47.37
157	2,3,3',4,4',5'-HxCB	157L	13C12-2,3,3',4,4',5'-HxCB	47.79
169L	13C12-3,3',4,4',5,5'-HxCB	138L	13C12-2,2',3,4,4',5'-HxCB	50.25
169	3,3',4,4',5,5'-HxCB	169L	13C12-3,3',4,4',5,5'-HxCB	50.25
178L	13C12-2,2',3,3',5,5',6-HpCB	—	13C12-2,2',4,5,5'-PeCB	42.88
180L	13C12-2,2',3,4,4',5,5'-HpCB	178L	13C12-2,2',3,3',5,5',6-HpCB	47.88
180	2,2',3,4,4',5,5'-HpCB	180L	13C12-2,2',3,4,4',5,5'-HpCB	47.88
170	2,2',3,3',4,4',5-HpCB	180L	13C12-2,2',3,4,4',5,5'-HpCB	49.90
189L	13C12-2,3,3',4,4',5,5'-HpCB	178L	13C12-2,2',3,3',5,5',6-HpCB	52.56
189	2,3,3',4,4',5,5'-HpCB	189L	13C12-2,3,3',4,4',5,5'-HpCB	52.56
209L	13C12-DCB[5]	178L	13C12-2,2',3,3',5,5',6-HpCB	56.63

[1] Suffix "L" indicates labeled compound.
[2] Retention time data are for HT-8 column (per manufacturer).
[3] Internal standards.
[4] Cleanup standard.
[5] Final eluter.

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Table 3. Concentrations of Stock and Spiking Solutions Containing the Native PCBs and Labeled Compounds

Cpd. No.	Compound	m/z type	Stock[3] (ng/mL)	Spiking Solution[2] (ng/mL)	Spiking Level (ng)
	Precision and Recovery Standards[1]				
1	3,3',4,4'-TCB	77	20	0.8	0.8
2	2,3,3',4,4'-PeCB	105	1000	40	40
3	2,3,4,4',5-PeCB	114	1000	40	40
4	2,3',4,4',5-PeCB	118	1000	40	40
5	2',3,4,4',5-PeCB	123	1000	40	40
6	3,3',4,4',5-PeCB	126	100	4	4
7	2,3,3',4,4',5-HxCB	156	1000	40	40
8	2,3,3',4,4',5'-HxCB	157	1000	40	40
9	2,3',4,4',5,5'-HxCB	167	1000	40	40
10	3,3',4,4',5,5'-HxCB	169	200	8	8
11	2,2',3,3',4,4',5-HpCB	170	200	8	8
12	2,2',3,4,4',5,5'-HpCB	180	1000	40	40
13	2,3,3',4,4',5,5'-HpCB	189	200	8	8
	Internal Standards[4]				
14	13C12-3,3',4,4'-TCB	77L	1000	50	50
15	13C12-2,3,3',4,4'-PeCB	105L	1000	50	50
16	13C12-2,3',4,4',5-PeCB	118L	1000	50	50
17	13C12-3,3',4,4',5-PeCB	126L	1000	50	50
18	13C12-2,3,3',4,4',5-HxCB	156L	1000	50	50
19	13C12-2,3,3',4,4',5'-HxCB	157L	1000	50	50
20	13C12-2,3',4,4',5,5'-HxCB	167L	1000	50	50
21	13C12-3,3',4,4',5,5'-HxCB	169L	1000	50	50
22	13C12-2,2',3,4,4',5,5'-HpCB	180L	1000	50	50
23	13C12-2,3,3',4,4',5,5'-HpCB	189L	1000	50	50
	Cleanup Standards[5]				
24	13C12-3,4,4',5-TCB	81L	200	10	10
25	13C12-2,3,3',5,5'-PeCB	111L	1000	50	50
	Recovery Standards[6]				
26	13C12-2,2',5,5'-TCB	52L	1000	1000	15
27	13C12-2,2',4,5,5'-PeCB	101L	1000	1000	15
28	13C12-2,2',3,4,4',5'-HxCB	138L	1000	1000	15
29	13C12-2,2',3,3',5,5',6-HpCB	178L	1000	1000	15
	Final Eluter				
30	13C12-DCB	209L	2000	100	100

[1] Section 7.6.7-prepared in nonane and diluted to prepare spiking solution.

[2] Sections 7.6.3.2, 7.6.4., 7.6.5, 7.6.7-prepared in acetone from stock solution daily.

[3] Section 7.6.1-prepared in nonane and diluted to prepare spiking solution. Concentrations are adjusted for expected background levels.

[4] Section 7.6.3.2-prepared in acetone from stock solution daily. Concentrations are adjusted for expected background levels.

[5] Section 7.6.4-prepared in acetone; added to sample extracts before cleanup.

[6] Section 7.6.5-prepared in nonane; added to concentrated extract prior to injection.

Table 4. Concentrations of PCBs in Calibration and Calibration Verification Solutions

	IUPAC No.[1]	CS1 (ng/mL)	CS2 (ng/mL)	CS3[2] (ng/mL)	CS4 (ng/mL)	CS5 (ng/mL)
Precision and Recovery Standards						
3,3',4,4'-TCB	77	0.5	2	10	40	200
2,3,3',4,4'-PeCB	105	2.5	10	50	200	1000
2,3,4,4',5-PeCB	114	2.5	10	50	200	1000
2,3',4,4',5-PeCB	118	2.5	10	50	200	1000
2',3,4,4',5-PeCB	123	2.5	10	50	200	1000
3,3',4,4',5-PeCB	126	2.5	10	50	200	1000
2,3,3',4,4',5-HxCB	156	5	20	100	400	2000
2,3,3',4,4',5'-HxCB	157	5	20	100	400	2000
2,3',4,4',5,5'-HxCB	167	5	20	100	400	2000
3,3',4,4',5,5'-HxCB	169	5	20	100	400	2000
2,2',3,3',4,4',5-HpCB	170	5	20	100	400	2000
2,2',3,4,4',5,5'-HpCB	180	5	20	100	400	2000
2,3,3',4,4',5,5'-HpCB	189	5	20	100	400	2000
Internal Standards	—					
13C12-3,3',4,4'-TCB	77L	100	100	100	100	100
13C12-2,3,3',4,4'-PeCB	105L	100	100	100	100	100
13C12-2,3',4,4',5-PeCB	118L	100	100	100	100	100
13C12-3,3',4,4',5-PeCB	126L	100	100	100	100	100
13C12-2,3,3',4,4',5-HxCB	156L	100	100	100	100	100
13C12-2,3,3',4,4',5'-HxCB	157L	100	100	100	100	100
13C12-2,3',4,4',5,5'-HxCB	167L	100	100	100	100	100
13C12-3,3',4,4',5,5'-HxCB	169L	100	100	100	100	100
13C12-2,2',3,4,4',5,5'-HpCB	180L	100	100	100	100	100
13C12-2,3,3',4,4',5,5'-HpCB	189L	100	100	100	100	100
Cleanup Standards						
13C12-3,4,4',5-TCB	81L	0.5	2	10	40	200
13C12-2,3,3',5,5'-PeCB	111L	2.5	10	50	200	1000
Recovery Standards						
13C12-2,2',5,5'-TCB	52L	100	100	100	100	100
13C12-2,2',4,5,5'-PeCB	101L	100	100	100	100	100
13C12-2,2',3,4,4',5'-HxCB	138L	100	100	100	100	100
13C12-2,2',3,3',5,5',6-HpCB	178L	100	100	100	100	100
Final Eluter						
13C12-DCB	209L	200	200	200	200	200

[1] Suffix "L" indicates labeled compound.
[2] Sections 7.6.6, calibration verification solution.

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Table 5. Labeled Compound Recovery in Samples When All PCBs are Tested

Labeled PCB	IUPAC No.	Test conc $(ng/mL)^1$	Labeled compound recovery	
			(ng/mL)	(%)
Internal Standards				
13C12-3,3',4,4'-TCB	77	100	20-160	20-160
13C12-2,3,3',4,4'-PeCB	105	100	20-160	20-160
13C12-2,3',4,4',5-PeCB	118	100	20-160	20-160
13C12-3,3',4,4',5-PeCB	126	100	20-160	20-160
13C12-2,3,3',4,4',5-HxCB	156	100	20-160	20-160
13C12-2,3,3',4,4',5'-HxCB	157	100	20-160	20-160
13C12-2,3',4,4',5,5'-HxCB	167	100	20-160	20-160
13C12-3,3',4,4',5,5'-HxCB	169	100	20-160	20-160
13C12-2,2',3,4,4',5,5'-HpCB	180	100	20-160	20-160
13C12-2,3,3',4,4',5,5'-HpCB	189	100	20-160	20-160
Cleanup Standards				
13C12-3,4,4',5-TCB	81	50	4-32	20-160
13C12-2,3,3',5,5'-PeCB	111	250	40-140	40-140

^{1} Based on 20 μL final extract volume.

Table 6. Descriptors, Exact m/z's, m/z Types, and Elemental Compositions of the PCBs

Descriptor	Exact m/z[1]	m/z type	Elemental composition	Substance[2]
1.	289.9224	M	C12 H6 35Cl4	TCB
	291.9194	M+2	C12 H6 35Cl3 37Cl	TCB
	301.9626	M	13C12 H6 35Cl4	TCB[3]
	303.9597	M+2	13C12 H6 35Cl3 37Cl	TCB[3]
	318.9792	Lock Mass	--	PFK
	325.8804	M+2	C12 H5 35Cl4 37Cl	PeCB
	327.8775	M+4	C12 H5 35Cl3 37Cl2	PeCB
	330.9793	Lock Mass Check	--	PFK
	337.9207	M+2	13C12 H5 35Cl4 37Cl	PeCB[3]
	339.9178	M+4	13C12 H5 35Cl3 37Cl2	PeCB[3]
2.	325.8804	M+2	C12 H5 35Cl4 37Cl	PeCB
	327.8775	M+4	C12 H5 35Cl3 37Cl2	PeCB
	337.9207	M+2	13C12 H5 35Cl4 37Cl	PeCB[3]
	339.9178	M+4	13C12 H5 35Cl3 37Cl2	PeCB[3]
	354.9792	Lock Mass	--	PFK
	354.9792	Lock Mass Check	--	PFK
	393.8025	M+2	C12 H3 35Cl6 37Cl	HpCB
	395.7996	M+4	C12 H3 35Cl5 37Cl2	HpCB
	405.8428	M+2	13C12 H3 35Cl6 37Cl	HpCB[3]
	407.8398	M+4	13C12 H3 35Cl5 37Cl2	HpCB[3]
3.	359.8415	M+2	C12 H4 35Cl5 37Cl	HxCB
	361.8385	M+4	C12 H4 35Cl4 37Cl2	HxCB
	371.8817	M+2	13C12 H4 35Cl5 37Cl	HxCB[3]
	373.8788	M+4	13C12 H4 35Cl4 37Cl2	HxCB[3]
	380.9760	Lock Mass	--	PFK
	380.9760	Lock Mass Check	--	PFK
	393.8025	M+2	C12 H3 35Cl6 37Cl	HpCB
	395.7996	M+4	C12 H3 35Cl5 37Cl2	HpCB
	405.8428	M+2	13C12 H3 35Cl6 37Cl	HpCB[3]
	407.8398	M+4	13C12 H3 35Cl5 37Cl2	HpCB[3]
4.	504.9696	Lock Mass	--	PFK
	504.9696	Lock Mass Check	--	PFK
	509.7229	M+4	13C12 35Cl8 37Cl2	DCB[3]
	511.7199	M+6	13C12 35Cl7 37Cl3	DCB[3]

[1] Nuclidic masses used were:
    H = 1.007825   C = 12.00000
    13C = 13.003355   35Cl = 34.968853   37Cl = 36.965903
[2] TCB   =   Tetrachlorobiphenyl
  PeCB =   Pentachlorobiphenyl
  HxCB =   Hexachlorobiphenyl
  HpCB =   Heptachlorobiphenyl
  DCB   =   Decachlorobiphenyl.
[3] 13C labeled compound.

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Table 7. Theoretical Ion Abundance Ratios and QC Limits

Chlorine atoms	m/z's forming ratio	Theoretical ratio	QC Limit[1]	
			Lower	Upper
4	M/(M+2)	0.77	0.65	0.89
5	(M+2)/(M+4)	1.55	1.32	1.78
6	(M+2)/(M+4)	1.24	1.05	1.43
7	(M+2)/(M+4)	1.05	0.88	1.20
10	(M+4)/(M+6)	1.17	0.99	1.35

[1] QC limits represent +/- 15 percent windows around the theoretical ion abundance ratio. These limits are preliminary.

Table 8. GC Retention Time Window Defining and Isomer Specificity Test Solution[1]
(Section 7.6.8)

Congener group	First eluted		Last eluted	
TCB	54	2,2',6,6'	77	3,3',4,4'
PeCB	104	2,2',4,6,6'	126	3,3',4,4',5
HxCB	155	2,2',4,4',6,6'	169	3,3',4,4',5,5'
HpCB	188	2,2',3,4',5,6,6'	189	2,3,3',4,4',5,5'

Isomer specificity test compounds

123	2',3,4,4',5-PeCB	156	2,3,3',4,4',5-HxCB
118	2,3',4,4',5-PeCB	157	2,3,3',4,4',5'-HxCB

[1] All compounds are at a concentration of 100 ng/mL in nonane.

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         ┌─────────────────────┐              ┌─────────────────────┐
         │ Sewage Sludge Sample│─────────────▶│  Determine Percent  │
         └─────────────────────┘              │ Moisture of 10 g    │
                    │                          │      aliquot        │
                    ▼                          └─────────────────────┘
         ┌─────────────────────┐
         │ Take 2 g Aliquot of │
         │   wet sample        │
         └─────────────────────┘
                    │
                    ▼
         ┌─────────────────────┐
         │ Spike with Labeled  │
         │ Internal Standards  │
         └─────────────────────┘
                    │
                    ▼
         ┌─────────────────────┐
         │ Mix with Drying     │
         │ Agent to Produce    │
         │   1:1 Ratio         │
         └─────────────────────┘
                    │
                    ▼
         ┌─────────────────────┐
         │  Soxhlet Extract    │
         └─────────────────────┘
                    │
                    ▼
         ┌─────────────────────┐              ┌─────────────────────┐
         │ Concentrate to 10 mL│─────────────▶│    Archive 5 mL     │
         └─────────────────────┘              └─────────────────────┘
                    │
                    ▼
         ┌─────────────────────┐
         │ Solvent Exchange    │
         │ 5 mL of Sample      │
         │ Extract to          │
         │ Hexane (50 mL)      │
         └─────────────────────┘
                    │
                    ▼
         ┌─────────────────────┐
         │ Spike with Cleanup  │
         │   Standard          │
         └─────────────────────┘
                    │
                    ▼
         ┌─────────────────────┐
         │ Proceed to Sample   │
         │ Cleanup Flow Diagram│
         │    (Figure 2)       │
         └─────────────────────┘
                    │
                    ▼
```

Figure 1. Sample Extraction Procedure for Sewage Sludge Sample

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                    ┌─────────────────────┐
                    │   See Figure 1 for  │
                    │   Description of    │
                    │   Sample Extraction │
                    └─────────────────────┘
                              │
                              ▼
                    ┌─────────────────────┐
                    │  Extract Hexane Extract │
                    │  with Sulfuric Acid*  │
                    └─────────────────────┘
                       │              │
            ┌──────────┘              └──────────┐
            ▼                                     ▼
   ┌─────────────────┐            ┌─────────────────────┐
   │  Discard the    │            │   Wash the Hexane   │
   │  Aqueous Layer  │            │     Layer with      │
   └─────────────────┘            │    NaCl Solution    │
                                  └─────────────────────┘
                                     │              │
                          ┌──────────┘              └──────────┐
                          ▼                                     ▼
                 ┌─────────────────┐            ┌─────────────────────┐
                 │  Discard the    │            │  Extract the Hexane │
                 │  Aqueous Layer  │            │        with         │
                 └─────────────────┘            │    KOH Solution     │
                                                └─────────────────────┘
                                                   │              │
                                        ┌──────────┘              └──────────┐
                                        ▼                                     ▼
                               ┌─────────────────┐            ┌─────────────────────┐
                               │  Discard the    │            │  Wash the Hexane    │
                               │  Aqueous Layer  │            │  Layer with NaCl    │
                               └─────────────────┘            │     Solution        │
                                                              └─────────────────────┘
                                                                 │              │
                                                      ┌──────────┘              └──────────┐
                                                      ▼                                     ▼
                                             ┌─────────────────┐            ┌──────────────┐
                                             │  Discard the    │            │     Dry      │
                                             │  Aqueous Layer  │            │ Extract with │ ──►
                                             └─────────────────┘            │   Na₂SO₄     │
                                                                            └──────────────┘
```

┌──────────────────┐
│ Sulfur Cleanup   │
│ Using Copper   │
└──────────────────┘
        │
        ▼
┌──────────────────┐
│ Silica Gel   │
│ Cleanup   │
└──────────────────┘
        │
        ▼
┌──────────────────┐
│ Carbon Column   │
│ Cleanup   │
└──────────────────┘
        │
        ▼
┌──────────────────┐
│ HPLC/GPC   │
│ Cleanup   │
└──────────────────┘
        │
        ▼
┌──────────────────┐
│ Concentrate   │
│ to Final Volume │
└──────────────────┘
        │
        ▼
┌──────────────────┐   ┌──────────────────┐
│ HRGC/HRMS   │ ◄── │ Add Recovery   │
│ Analyses   │   │ Standard Solution│
└──────────────────┘   └──────────────────┘

* Repeat this step until the
aqueous layer is clear

Figure 2. Sample Cleanup Procedure for Sewage Sludge Sample

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N-1-3
Draft Scrubber Water Method

Proposed Analytical Method

Determination of Toxic Polychlorinated Biphenyls in Sewage
Incinerator Scrubber Water using Isotope Dilution High Resolution
Gas Chromatography/High Resolution Mass Spectrometry

July 20, 1999

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Proposed Analytical Method for Determination of Toxic Polychlorinated Biphenyls in Sewage Incinerator Scrubber Water by Isotope Dilution High Resolution Gas Chromatography/High Resolution Mass Spectrometry

1.0   SCOPE AND APPLICATION

1.1   This analytical method is for determination of the toxic polychlorinated biphenyls (PCBs) in sewage incinerator scrubber water by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The method is for use in the Emission Measurement Center's (EMC) data gathering effort to support a Maximum Achievable Control Technology (MACT) standard to limit emissions of hazardous air pollutants at two sewage sludge incinerators. The method is based on a compilation of methods from the technical literature, and EPA Method 1668 (References 1-14).

1.2   The toxic PCBs listed in Table 1 may be determined by this method.

1.3   The detection limits and quantitation levels listed in this method may be dependent on the level of interferences rather than instrumental limitations.

1.4   The HRGC/HRMS portions of this method are for use only by analysts experienced with HRGC/HRMS, or under the close supervision of such qualified persons.

2.0   SUMMARY OF METHOD

2.1   Extraction

An analytical flow diagram depicting the scrubber water extraction procedure is shown in Figure 1.

2.1.1   Scrubber water samples (samples containing ≤ 5% solids upon visual inspection)

2.1.1.1   Stable isotopically labeled analogs of the toxic PCBs are spiked into a 1 L sample, and the sample is vacuum-filtered through a C_{18} solid-phase extraction (SPE) column.

2.1.1.2   The column is eluted with acetone and methylene chloride, the eluant is concentrated for cleanup and spiked with cleanup standard.

2.1.2   Scrubber water samples (samples containing > 5% solids upon visual inspection)

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2.1.2.1   A 1 L aliquot of the sample is filtered; the filtrate is spiked with stable isotopically labeled analogs of the toxic PCBs, and the sample is vacuum-filtered through a C_{18} solid-phase extraction (SPE) column.

2.1.2.2   The column is eluted with acetone and methylene chloride.

2.1.2.3   The solids are extracted using the Soxhlet technique, and the filtrate extract and the solids extract are combined, concentrated, and spiked with cleanup standards.

2.2   An analytical flow diagram depicting the scrubber water cleanup procedure is shown in Figure 2. The scrubber water extract is cleaned using acid and base partitioning, and silica gel and activated carbon chromatography.

2.3   After cleanup, the extract is concentrated to a final volume between 20 μL - 1.0 mL, per the analyst's discretion. Prior to injection recovery standards are added to each extract, and an aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a high resolution mass spectrometer. Two exact m/z's are monitored for each analyte.

2.4   An individual PCB congener is identified by comparing the GC retention time and ion-abundance ratio of two exact m/z's with the corresponding retention time of an authentic standard and the theoretical or acquired ion-abundance ratio of the two exact m/z's. Isomer specificity for the toxic PCBs is achieved using GC columns that resolve these congeners from the other PCBs.

2.5   Results are quantified using relative response factors.

2.6   The quality of the analysis is assured through reproducible calibration and verification of operation for the extraction, cleanup, and GC/MS systems.

3.0   DEFINITIONS AND ABBREVIATIONS

3.1   Definitions and Acronyms

3.1.1   **Analyte** – a PCB compound measured by this method. The analytes are listed in Table 1.

3.1.2   **Calibration Standard (CS)** – a solution prepared from a secondary standard and/or stock solutions and used to calibrate the response of the instrument with respect to analyte concentration.

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3.1.3 **Calibration Verification Standard (VER)** – the mid-point calibration standard (CS3) that is used to verify calibration (see Table 4).

3.1.4 **Congener** – refers to a particular compound of the same chemical family.

3.1.5 **CS1, CS2, CS3, CS4, CS5** – see calibration standards in Table 4.

3.1.6 **Field Blank** – an aliquot of reagent water or other reference matrix that is placed in a sample container in the laboratory or the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

3.1.7 **HRGC** – high resolution gas chromatography or gas chromatograph.

3.1.8 **HRMS** – high resolution mass spectrometry or mass spectrometer.

3.1.9 **Internal Standard (IS)** – a component which is added to every sample and is present in the same concentration in every blank, quality control sample, and calibration solution. The IS is added to the sample before extraction and is used to measure the concentration of the analyte and surrogate compound. The IS recovery serves as an indicator of the overall performance of the analysis.

3.1.10 **K-D** – Kuderna-Danish concentrator; a device used to concentrate the analytes in a solvent.

3.1.11 **Laboratory Blank** – see Laboratory Method Blank.

3.1.12 **Laboratory Method Blank** – an aliquot of reagent water or solvent that is treated exactly as a sample including exposure to all laboratory glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The laboratory method blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

3.1.13 **Laboratory Spike Sample** – a laboratory-prepared matrix blank spiked with known quantities of analytes. The laboratory spike sample is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in the method for precision and recovery.

3.1.14 **May** – this action, activity, or procedural step is neither required nor prohibited.

3.1.15 **May not** – this action, activity, or procedural step is prohibited.

3.1.16 **Must** – this action, activity, or procedural step is required.

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3.1.17 **m/z Scale** – the molecular mass to charge ratio scale.

3.1.18 **PAR** – precision and recovery standard; secondary standard used to prepare laboratory spike samples.

3.1.19 **Percent Relative Standard Deviation (%RSD)** – the standard deviation times 100 divided by the mean. Also termed "coefficient of variation."

3.1.20 **PFK** – perfluorokerosene; the mixture of compounds used to calibrate the exact m/z scale in the HRMS.

3.1.21 **Primary Dilution Standard** – a solution containing the specified analytes that is purchased or prepared from stock solutions and diluted as needed to prepare calibration solutions and other solutions.

3.1.22 **QC Check Sample** – a sample containing all or a subset of the analytes at known concentrations. The QC check sample is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

3.1.23 **Reagent Water** – water demonstrated to be free from the analytes of interest and potentially interfering substances at the analyte estimated detection limit; e.g., HPLC grade water.

3.1.24 **Recovery Standard** – a known amount of component added to the concentrated sample extract before injection. The response of the internal standards relative to the recovery standard is used to estimate the overall recovery of the internal standards.

3.1.25 **Relative Response Factor** – the response of the mass spectrometer to a known amount of an analyte relative to a known amount of an internal standard.

3.1.26 **RF** - response factor (see Section 10.2.2).

3.1.27 **RPD** – relative percent difference, defined as the absolute value of the difference between two values divided by the mean of the two values, expressed as a percentage.

3.1.28 **S/N** – signal to noise ratio.

3.1.29 **Should** – this action, activity, or procedural step is suggested but not required.

3.1.30 **SiCP** – selected ion current profile; the line described by the signal at an exact m/z.

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3.1.31 **SPE** – solid-phase extraction; an extraction technique in which an analyte is extracted from an aqueous sample by passage over or through a material capable of reversibly adsorbing the analyte. Also termed liquid-solid extraction.

3.1.32 **Specific Isomers** – a specific isomer is designated by indicating the exact positions (carbon atoms) where chlorines are located within the molecule. For example, 2,3,3',4,4'-PeCB refers to only one of the 209 possible PCB isomers - that isomer which is chlorinated in the 2,3,3',4,4'-position of the biphenyl ring structure.

3.1.33 **Specificity** – the ability to measure an analyte of interest in the presence of interferences and other analytes of interest encountered in a sample.

3.1.34 **Stock Solution** – a solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

3.1.35 **Toxic PCB** – any or all of the toxic chlorinated biphenyl isomers shown in Table 1.

3.1.36 **VER** – see Calibration Verification Standard (Section 3.1.3).

3.2 Abbreviations

3.2.1 **PCB** – any or all of the 209 possible polychlorinated biphenyl isomers.

3.2.2 **TCB** – abbreviation for tetrachlorinated biphenyl.

3.2.3 **PeCB** – abbreviation for pentachlorinated biphenyl.

3.2.4 **HxCB** – abbreviation for hexachlorinated biphenyl.

3.2.5 **HpCB** – abbreviation for heptachlorinated biphenyl.

3.2.6 **DCB** – abbreviation for decachlorinated biphenyl.

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4.0   CONTAMINATION AND INTERFERENCES

4.1   Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated backgrounds at the ions monitored. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing field and laboratory blanks as described in Sections 9.1.1 and 9.2.2.

4.2   Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, reagents are cleaned by extraction or solvent rinsing. The toxic PCB congeners 105, 114, 118, 123, 156, 157, 167, and 180 have been shown to be very difficult to completely eliminate from the laboratory, and baking of glassware in a kiln or furnace at 450-500°C may be necessary to remove these and other contaminants.

4.3   Proper cleaning of glassware is extremely important because glassware may not only contaminate the samples but may also remove the analytes of interest by adsorption onto the glass surface.

   4.3.1   Glassware should be rinsed with methanol and washed with a detergent solution as soon after use as is practical. Sonication of glassware containing a detergent solution for approximately 30 seconds may aid in cleaning. Glassware with removable parts, particularly separatory funnels with fluoropolymer stopcocks, must be disassembled prior to detergent washing.

   4.3.2   After detergent washing, glassware should be rinsed immediately; first with methanol, then with hot tap water. The tap water rinse is followed by distilled water, methanol, and then methylene chloride rinses.

   4.3.3   Baking of glassware in kiln or other high temperature furnace (450-500°C) may be warranted after particularly dirty samples are encountered. However, baking should be minimized, as repeated baking of glassware may cause active sites on the glass surface that may irreversibly adsorb PCBs.

   4.3.4   Immediately prior to use, the Soxhlet apparatus should be pre-extracted with methylene chloride for 3 hours to remove any possible background contamination.

4.4   The use of high purity reagents minimizes background contamination and interference problems. Purification of solvents by distillation in all-glass systems may be required.

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4.5   Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences may vary considerably with the source being sampled. Toxic PCBs are often associated with other interfering chlorinated compounds which are at concentrations several orders of magnitude higher than that of the PCBs of interest. The cleanup procedures in Section 11.3 can be used to reduce many of these interferences, but unique samples may require additional cleanup approaches.

4.6   Two high resolution capillary columns, a J&W DBXLB, 60 m x 0.25 mm x 0.25 μm (J&W), and a 50 m x 0.23 mm x 0.25 μm HT-8 (SGE), are recommended for PCB analysis because both of these columns will resolve all 13 toxic PCBs. Equivalent columns that sufficiently resolve the toxic PCBs may also be used.

4.7   If other gas chromatographic conditions or other techniques are used, the analyst is required to support the data through an adequate quality assurance program.

5.0   SAFETY

5.1   The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Nevertheless, each chemical compound should be treated as a potential health hazard. Therefore, exposure to these chemicals must be reduced to the lowest possible level by whatever means available.

5.2   The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis.

5.3   PCBs and methylene chloride have been classified as known or suspected human or mammalian carcinogens.

5.4   Unsterilized sewage incinerator scrubber water may be a human health risk because pathogens contained within the sample, e.g., salmonella, E. coli, hepatitis, may be aerosolized and transported to the human host via inhalation or dermal contact with mucous membranes. Scrubber water samples that have not been pre-treated with chlorine (minimum of 4 ppmv) should be sterilized by adding 4% (v/v) nitric acid to the sampling bottles prior to collection in the field (see Section 8.2).

6.0   APPARATUS, EQUIPMENT, AND SUPPLIES

6.1   Glassware Cleaning Equipment—Laboratory sink with overhead fume hood.

6.2   Sample Preparation Equipment

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6.2.1 Laboratory fume hood of sufficient size to contain the sample preparation equipment listed below.

6.2.2 Glove box (optional).

6.2.3 Equipment for determining percent solids

    6.2.3.1 Oven – For determining percent solids; capable of maintaining a temperature of $110 \pm 5°C$.

    6.2.3.2 Desiccator.

6.2.4 Balances

    6.2.4.1 Analytical – Capable of weighing 0.1 mg.

    6.2.4.2 Top loading—Capable of weighing 10 mg.

6.3 Extraction Apparatus

6.3.1 Graduated cylinder, 1-L capacity.

6.3.2 Solid-phase extraction

    6.3.2.1 Solid phase extraction manifold.

    6.3.2.2 Vacuum source capable of maintaining 25 in. Hg, equipped with shutoff valve and vacuum gauge.

    6.3.2.3 Solid-phase extraction cartridge containing octadecyl (C_{18}) bonded silica uniformly enmeshed in an inert matrix—Fisher Scientific 14-378F (or equivalent).

6.3.3 Soxhlet Apparatus

    6.3.3.1 Soxhlet – 50-mm ID, 200-mL capacity with 500-mL flask (Cal-Glass LG-6900, or equivalent, except substitute 500-mL round-bottom flask for 300-mL flat-bottom flask).

    6.3.3.2 Thimble – 43 mm × 123 mm to fit Soxhlet (Cal-Glass LG-6901-122, or equivalent).

    6.3.3.3 Heating mantle – Hemispherical, to fit 500-mL round-bottom flask (Cal-Glass LG-8801-112, or equivalent).

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6.3.3.4   Variable transformer – Powerstat (or equivalent), 110-volt, 10-amp.

6.3.4   Beakers – 400- to 500-mL.

6.3.5   Spatulas – Stainless steel.

6.4   Filtration Apparatus

6.4.1   Pyrex glass wool – heated in an oven at 450-500°C for 8 hours minimum.

6.4.2   Glass funnel – 125- to 250-mL.

6.4.3   Glass-fiber or quartz fiber filter paper – Whatman GF/D (or equivalent).

6.4.4   Drying column – 15- to 20-mm ID Pyrex chromatographic column equipped with coarse-glass frit or glass-wool plug.

6.4.5   Pressure filtration SPE manifold, Supelco or equivalent.

6.5   Cleanup Apparatus

6.5.1   Pipets

6.5.1.1   Disposable, Pasteur, 150-mm long × 5-mm ID (Fisher Scientific 13-678-6A, or equivalent).

6.5.1.2   Disposable, serological, 50-mL (8- to 10- mm ID).

6.5.2   Glass chromatographic columns

6.5.2.1   150-mm long × 8-mm ID, (Kontes K-420155, or equivalent) with coarse-glass frit or glass-wool plug and 250-mL reservoir.

6.5.2.2   200-mm long × 15-mm ID, with coarse-glass frit or glass-wool plug and 250-mL reservoir.

6.5.2.3   300-mm long x 22-mm ID, with coarse-glass frit, 300-mL reservoir, and glass or fluoropolymer stopcock.

6.5.3   Oven – For baking and storage of adsorbents, capable of maintaining a constant temperature (±5°C) in the range of 105-250°C.

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6.6   Concentration Apparatus

6.6.1   Rotary evaporator – Buchi/Brinkman-American Scientific No. E5045-10 or equivalent, equipped with a variable temperature water bath.

6.6.1.1   Vacuum source for rotary evaporator equipped with shutoff valve at the evaporator and vacuum gauge.

6.6.1.2   A recirculating water pump and chiller are recommended, as use of tap water for cooling the evaporator wastes large volumes of water and can lead to inconsistent performance as water temperatures and pressures vary.

6.6.1.3   Round-bottom flask – 100-mL and 500-mL or larger, with ground-glass fitting compatible with the rotary evaporator.

6.6.2   Kuderna-Danish (K-D) concentrator

6.6.2.1   Concentrator tube – 10-mL, graduated (Kontes K-570050-1025, or equivalent) with calibration verified. Ground-glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

6.6.2.2   Micro concentrator tube – 1.0-mL, graduated (Kontes K-570050-1000, or equivalent) with calibration verified. Ground-glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

6.6.2.3   Evaporation flask – 500-mL (Kontes K-570001-0500, or equivalent), attached to concentrator tube with springs (Kontes K-662750-0012 or equivalent).

6.6.2.4   Snyder column – Three-ball macro (Kontes K-503000-0232, or equivalent).

6.6.2.5   Boiling chips.

6.6.2.5.1   Glass or silicon carbide – Approximately 10/40 mesh, extracted with methylene chloride and baked at 450°C for 1 hour minimum.

6.6.2.5.2   Fluoropolymer (optional) – Extracted with methylene chloride.

6.6.2.6   Water bath – Heated, with concentric ring cover, capable of maintaining a temperature within ±2°C, installed in a fume hood.

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6.6.3 Nitrogen blowdown apparatus – Equipped with water bath controlled in the range of 30 - 60°C (N-Evap, Organomation Associates, Inc., or equivalent), installed in a fume hood.

6.6.4 TurboVap Nitrogen blowdown apparatus – Equipped with Turbotubes, and water bath controlled in the range of 30 - 60°C (Turbovap II, Zymark, or equivalent).

6.6.5 Sample vials

6.6.5.1 Amber glass, 2- to 5-mL with fluoropolymer-lined screw cap.

6.6.5.2 Glass, 0.3-mL, conical, with fluoropolymer-lined screw or crimp cap.

6.7 Gas Chromatograph – Shall have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and shall meet all of the performance specifications in Section 10.

6.7.1 GC Columns – Each of the GC columns listed below is capable of resolving the 13 toxic PCB congeners analyzed for in this method. Other GC columns may be used when resolution of the PCB congeners of concern from their most closely eluting leading and trailing congeners can be demonstrated.

6.7.2 Column #1—50 m long × 0.25±0.02-mm ID; 0.25-μm film HT-8 (SGE, or equivalent).

6.7.3 Column #2—60 m long × 0.25±0.02-mm ID; 0.25-μm film DBXLB (J&W, or equivalent).

6.8 High Resolution Mass Spectrometer – 28- to 40-eV electron impact ionization, shall be capable of repetitively selectively monitoring 12 exact m/z's minimum at high resolution ($\geq 10,000$) during a period less than 1.5 seconds, and shall meet all of the performance specifications in Section 10.

6.9 HRGC/HRMS Interface – The high resolution mass spectrometer (HRMS) shall be interfaced to the high resolution gas chromatograph (HRGC) such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beams.

6.10 Data System – Capable of collecting, recording, and storing MS data.

7.0 REAGENTS AND STANDARDS

Note: unless otherwise stated, all reagents, water, and solvents must be pesticide grade (if available) or equivalent.

7.1 Acid and Base Partitioning

7.1.1 Potassium hydroxide – Dissolve 20 g pesticide grade (if available) KOH in 100 mL reagent water.

7.1.2 Sulfuric acid – Pesticide grade (if available; specific gravity 1.84).

7.1.3 Hydrochloric acid – Pesticide grade (if available), 6N.

7.1.4 Sodium chloride – Pesticide grade (if available), prepare at 5% (w/v) solution in reagent water.

7.2 Solution Drying and Evaporation

7.2.1 Solution drying – Sodium sulfate, reagent grade, granular, anhydrous (Baker 3375, or equivalent), rinsed with methylene chloride (20 mL/g), baked at 400°C for 1 hour minimum, cooled in a desiccator, and stored in a pre-cleaned glass bottle with screw-cap that prevents moisture from entering. If, after heating, the sodium sulfate develops a noticeable grayish cast (due to the presence of carbon in the crystal matrix), that batch of reagent is not suitable for use and should be discarded. Extraction with methylene chloride (as opposed to simple rinsing) and baking at a lower temperature may produce sodium sulfate that is suitable for use.

7.2.2 Prepurified nitrogen – 99.9995% purity.

7.2.3 Desiccant – EM Science silica gel Grade H Type IV Indicating (6-16 mesh).

7.3 Extraction

7.3.1 Solvents – Acetone, n-hexane, methanol, methylene chloride, and nonane; distilled in glass, pesticide quality, lot-certified to be free of interferences.

7.3.2 Water – Pesticide grade or equivalent, sold and stored in glass containers.

7.4 Adsorbents for Sample Cleanup

7.4.1 Silica gel

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7.4.1.1 Activated silica gel – 100-200 mesh, Supelco 1-3651 (or equivalent), rinsed with methylene chloride, baked at 180°C for a minimum of 1 hour, cooled in a desiccator, and stored in a precleaned glass bottle with screw-cap that prevents moisture from entering.

7.4.1.2 Acid silica gel (30% w/w) – Thoroughly mix 44 g of concentrated sulfuric acid with 100 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a screw-capped bottle with fluoropolymer-lined cap.

7.4.1.3 Basic silica gel – Thoroughly mix 30 g of 1N sodium hydroxide with 100 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a screw-capped bottle with fluoropolymer-lined cap.

7.4.2 Carbon

7.4.2.1 Carbopak C – (Supelco 1-0258, or equivalent).

7.4.2.2 Celite 545 – (Supelco 2-0199, or equivalent).

7.4.2.3 Thoroughly mix 18 g Carbopak C and 18 g Celite 545 to produce a 50% w/w mixture. Activate the mixture at 130°C for a minimum of 6 hours. Store in a desiccator.

7.5 Standard Solutions

Standards purchased as solutions or mixtures with certification to their purity, concentration, and authenticity, or prepared from materials of known purity and composition. If the chemical purity is 98 percent or greater, the weight may be used without correction to compute the concentration of the standard. Standards should be stored in the dark in a freezer at $\leq 0°C$ in screw-capped vials with fluoropolymer-lined caps when not being used. A mark is placed on the vial at the level of the solution so that solvent loss by evaporation can be detected. If solvent loss has occurred, or the shelf life has expired, the solution should be replaced.

7.5.1 Stock Standard Solutions

7.5.1.1 Prepared in nonane per the steps below or purchase as dilute solutions (Cambridge Isotope Laboratories/CIL, Woburn, MA, or equivalent). Observe the safety precautions in Section 5.

7.5.1.2 An appropriate amount of assayed reference material is dissolved in solvent. For example, weigh 1 to 2 mg of PCB 126 to three significant figures in a 10-mL ground-glass-stoppered volumetric flask and fill to

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the mark with nonane. After the PCB is completely dissolved, transfer the solution to a clean 15-mL vial with fluoropolymer-lined cap.

7.5.1.3 Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards. Reference standards that can be used to determine the accuracy of calibration standards are available from several vendors.

7.5.2 Precision and Recovery (PAR) Stock Solution

Using the solutions in Section 7.5, prepare the PAR stock solution to contain the PCBs of interest at the concentrations shown in Table 3. When diluted, the solution will become the PAR spiking solution (Section 7.5.7).

7.5.3 Internal Standard Solutions

7.5.3.1 Internal Standard Stock Solution

From stock standard solutions, or from purchased mixtures, prepare the solution to contain the labeled internal standards in nonane at the stock solution concentrations shown in Table 3. This solution is diluted with acetone prior to use (Section 7.5.3.2).

7.5.3.2 Internal Standard Spiking Solution

Dilute a sufficient volume of the labeled internal standard stock solution (Section 7.5.3.1) by a factor of 500 with acetone to prepare a diluted spiking solution. Concentrations may be adjusted to compensate for background levels. Each sample requires 1.0 mL of the diluted solution.

7.5.4 Cleanup Standard Spiking Solution

7.5.4.1 Prepare labeled PCBs 81 and 111 in acetone at the level shown in Table 3.

7.5.4.2 The cleanup standard is added to the scrubber water extract prior to cleanup to measure the efficiency of the cleanup process.

7.5.5 Recovery Standard(s) Spiking Solution

Prepare the recovery standard spiking solution to contain labeled PCBs 52, 101, 139, and 178 in nonane at the level shown in Table 3.

7.5.6 Calibration Standards (CS1 through CS5)

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7.5.6.1 Combine the solutions in Sections 7.5.1 to produce the five calibration solutions shown in Table 4 in nonane.

7.5.6.2 Calibration standards may also be purchased already prepared in nonane (CIL). ·

7.5.6.3- These solutions permit the relative response factor (labeled to native) to be measured as a function of concentration. The CS3 standard is used for calibration verification (VER).

7.5.7 Precision and Recovery (PAR) Spiking Solution

7.5.7.1 Used for preparation of laboratory spike duplicate samples (Section 9.5).

7.5.7.2 Dilute 200 µL of the PAR stock solution (Section 7.5.2) to 10 mL with acetone. Each laboratory spike QC sample requires 1.0 mL.

7.5.8 GC Retention Time Window Defining and Isomer Specificity Test Solution

7.5.8.1 This solution is used to define the beginning and ending retention times for the PCB congeners and to demonstrate isomer specificity of the GC columns.

7.5.8.2 The solution must contain the compounds listed in Table 8 (CIL, or equivalent), at a minimum.

7.5.9 QC Check Sample

If available, a QC check sample should be obtained from a source independent of the calibration standards. Ideally, this check sample would be a certified standard reference material (SRM) containing the PCBs in known concentrations in a sample matrix similar to the matrix being analyzed.

7.5.10 Solution Stability

7.5.10.1 Standard solutions used for quantitative purposes (Section 7.5.6) should be analyzed periodically, and should be assayed against reference standards before further use.

7.5.10.2 If the analysis yields standard concentrations that are not within 25% of the true value for any PCB, the solutions will be replaced with solutions that, when analyzed, yield concentrations that are within 25% of the true value.

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8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE, AND HOLDING TIMES

8.1 Sample Collection

Scrubber water samples are collected as grab samples.

8.2 Pre-Treatment/Sterilization

Sample bottle must contain enough 1:1 HNO_3 to give 4% HNO_3 (v/v) for sterilization if the scrubber water is not pre-treated with chlorine (minimum of 4 ppmv).

8.3 Sample Storage

Maintain aqueous samples in the dark at 4°C from the time of collection until receipt at the laboratory.

8.4 Holding Times

8.4.1 Samples are stored in the dark at 4°C.

8.4.2 Sample extracts are stored in the dark at <-10°C until analyzed.

8.4.3 A maximum of 30 days between sample collection and extraction, and a maximum of 45 days between extraction and analysis is recommended.

9.0 QUALITY ASSURANCE/QUALITY CONTROL

9.1 The minimum requirements of this method consist of spiking samples with labeled compounds to evaluate and document analyte recovery, and preparation and analysis of QC samples including blanks and duplicates. Laboratory performance is compared to target performance criteria to establish the performance requirements of the method.

9.2 Labeled Compounds

The laboratory shall spike all samples with the labeled standard spiking solutions (Sections 7.5.3.2 and 7.5.4) to assess method performance on the sample matrix. Recovery of labeled standards from samples should be assessed and records should be maintained.

9.2.1 Analyze each sample according to the procedures in Section 11. Compute the percent recovery of the labeled standards as described in Section 12.2.3.

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9.2.2 The recovery of each labeled compound will be compared to the target limits in Table 5. If the recovery of any compound falls outside of these limits, the data will be flagged and impact on reported concentration will be discussed in the reported results.

9.3 Laboratory Method Blanks

9.3.1 Prepare, extract, clean up, and concentrate a laboratory method blank with each sample batch (samples of the same matrix started through the extraction process on the same 12-hour shift, to a maximum of 20 samples).

9.3.2 If any native PCB analytes (Table 1) are found in the blank at greater than 20 percent of the concentration level found in the sample, the reported data should be flaggged as potentially containing some contribution from laboratory procedures. If method blank contamination is severe, sample preparation and analysis procedures should be reviewed and reprocessing the sample set should be considered depending on specific project requirements.

9.4 QC Check Sample

If available, analyze a QC check sample (Section 7.6.9) periodically to assure the accuracy of calibration standards and the overall reliability of the analytical process. It is suggested that the QC check sample be analyzed at least quarterly.

9.5 Laboratory Spike Duplicates

9.5.1 With each sample batch, spike duplicate scrubber water samples with PAR spiking solution (Section 7.6.7) and process through extraction, cleanup, and analysis procedures as the field samples.

9.5.2 Calculate precision for the duplicate laboratory spike samples as the relative percent difference (RPD). The RPD should be ≤ 50 percent.

9.5.3 Calculate accuracy for the laboratory spike samples by determining the percent recovery of spiked analytes. Accuracy should be within 40 - 160 percent for analytes spiked five times the background level of the scrubber water samples.

9.6 Method Specifications

9.6.1 The specifications contained in this method can be met if the apparatus used is calibrated properly and then maintained in a calibrated state.

9.6.2 The standards used for calibration (Section 7.6.6), calibration verification (Section 7.6.6.3), and for laboratory spike samples (Section 7.6.7) should be identical, so that the most precise results will be obtained.

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9.6.3   A HRGC/HRMS instrument will provide the most reproducible results if dedicated to the settings and conditions required for the analyses of PCB analytes by this method.

10.0   HRGC/HRMS CALIBRATION

10.1   Operating Conditions

Establish the operating conditions necessary to meet the minimum retention times for the internal and recovery standards in Table 2.

10.1.1   Suggested HRGC Operating Conditions

Injector temperature: 290°C
Interface temperature: 290°C
Initial temperature: 150°C
Initial time: 2 min
Temperature program: 150 to 200°C at 10°C/min; 200 to 280°C at 2°C/min

NOTE: All portions of the column that connect the HRGC to the ion source shall remain at or above the interface temperature specified above during analysis to preclude condensation of less volatile compounds.

The HRGC conditions may be optimized for compound separation and sensitivity. Once optimized, the same HRGC conditions must be used for the analysis of all standards, blanks, and samples.

10 1.2   High Resolution Mass Spectrometer (HRMS) Resolution

10.1.2.1   Obtain a selected ion current profile (SICP) of each analyte listed in Table 3 at the two exact m/z's specified in Table 6 and at ≥10,000 resolving power by injecting an authentic standard of the PCBs either singly or as part of a mixture in which there is no interference between closely eluted components.

10.1.2.2   The analysis time for PCBs may exceed the long-term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, a mass-drift correction is mandatory and a lock-mass m/z from PFK is used for drift correction. The lock-mass m/z is dependent on the exact m/z's monitored within each descriptor, as shown in Table 6. The level

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of PFK metered into the HRMS during analyses should be adjusted so that the amplitude of the most intense selected lock-mass m/z signal (regardless of the descriptor number) does not exceed 10 percent of the full-scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

NOTE: Excessive PFK (or any other reference substance) may cause noise problems and contamination of the ion source necessitating increased frequency of source cleaning.

10.1.2.3 If the HRMS has the capability to monitor resolution during the analysis, it is acceptable to terminate the analysis when the resolution falls below 10,000 to save reanalysis time.

10.1.2.4 Using a PFK molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 (10 percent valley) at m/z 380.9760. For each descriptor (Table 6), monitor and record the resolution and exact m/z's of three to five reference peaks covering the mass range of the descriptor. The resolution must be greater than or equal to 10,000, and the deviation between the exact m/z and the theoretical m/z (Table 6) for each exact m/z monitored must be less than 5 ppm.

10.1.3 Ion Abundance Ratios, Minimum Levels, Signal-to-Noise Ratios, and Absolute Retention Times

10.1.3.1 Choose an injection volume of either 1- or 2-µL, consistent with the capability of the HRGC/HRMS instrument. Inject a 1- or 2-µL aliquot of the CS1 calibration solution (Table 4) using the GC conditions from Section 10.1.1.

10.1.3.2 Measure the SICP areas for each analyte, and compute the ion abundance ratios at the exact m/z's specified in Table 6. Compare the computed ratio to the theoretical ratio given in Table 7.

The exact m/z's to be monitored in each descriptor are shown in Table 6. Each group or descriptor shall be monitored in succession as a function of GC retention time to ensure that all of the toxic PCBs are detected. Additional m/z's may be monitored in each descriptor, and the m/z's may be divided among more than the descriptors listed in Table 6, provided that the laboratory is able to monitor the m/z's of all the PCBs that may elute from the GC in a given retention-time window.

The mass spectrometer shall be operated in a mass-drift correction mode, using PFK to provide lock m/z's. The lock mass for each group

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of m/z's is shown in Table 6. Each lock mass shall be monitored and shall not vary by more than ±20 percent throughout its respective retention time window. Variations of the lock mass by more than 20 percent indicate the presence of coeluting interferences that may significantly reduce the sensitivity of the mass spectrometer. Reinjection of another aliquot of the sample extract will not resolve the problem. Additional cleanup of the extract may be required to remove the interferences.

10.1.3.3 All PCB analytes and labeled compounds in the CS1 standard shall be within the QC limits in Table 7 for their respective ion abundance ratios; otherwise, the mass spectrometer shall be adjusted and this test repeated until the m/z ratios fall within the limits specified. If the adjustment alters the resolution of the mass spectrometer, resolution shall be verified (Section 10.1.2) prior to repeat of the test.

10.1.3.4 The peaks representing the PCBs and labeled compounds in the CS1 calibration standard must have signal-to-noise ratios (S/N) greater than or equal to 10.0. Otherwise, the mass spectrometer shall be adjusted and this test repeated until the peaks have S/N greater than or equal to 10.0.

10.1.3.5 Retention Time Windows – Analyze the GC retention time window defining and isomer specificity test solution (Section 7.5.8) using the optimized temperature program in Section 10.1.1. Table 2 gives the elution order (first/last) of the window-defining compounds.

10.1.4 Isomer Specificity

10.1.4.1 From the analysis of the GC retention time window and isomer specificity test solution (Section 10.1.3.5), compute the percent valley between the GC peaks for PCB 123 and PCB 118, and between the GC peaks for PCB 156 and 157.

10.1.4.2 Verify that the height of the valley between these closely eluted isomers is less than 25 percent. If the valley exceeds 25 percent, adjust the analytical conditions and repeat the test or replace the GC column and recalibrate.

10.2 Initial Calibration

10.2.1 Prepare a calibration curve encompassing the concentration range for each compound to be determined. Referring to Table 2, calculate the relative response factors for unlabeled target analytes (RF_n) relative to their appropriate internal standard (Table 5) and the relative response factors for the $^{13}C_{12}$-labeled internal

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standards (RF_{is}) using the four recovery standards (Table 5) according to the following formulae:

$$RF_n = \frac{(A_n^{\ 1} + A_n^{\ 2}) \times Q_{rs}}{(A_{is}^{\ 1} + A_{is}^{\ 2}) \times Q_n}$$

$$RF_{is} = \frac{(A_{is}^{\ 1} + A_{is}^{\ 2}) \times Q_{rs}}{(A_n^{\ 1} + A_n^{\ 2}) \times Q_{is}}$$

where:

$A_n^{\ 1}$ and $A_n^{\ 2}$	=	*sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and 6) for unlabeled PCBs,*
$A_{is}^{\ 1}$ and $A_{is}^{\ 2}$	=	*sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and 6) for the labeled internal standards,*
$A_n^{\ 1}$ and $A_n^{\ 2}$	=	*sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and 6) for the recovery standard,*
Q_{is}	=	*quantity of the internal standard injected (pg),*
Q_n	=	*quantity of the recovery standard injected (pg), and*
Q_n	=	*quantity of the unlabeled PCB analyte injected (pg).*

RF_n and the RF_{is} are dimensionless quantities; the units used to express Q_{is}, Q_n, and Q_n must be the same.

10.2.2 Calculate the mean relative response factors and their respective percent relative standard deviation (%RSD) for the five calibration solutions. If the mean relative response factors between the analytes is not within 35% RSD, the instrument must be re-calibrated.

$$\overline{RF_n} = \frac{\sum_{j=1}^{5} RF_{n(j)}}{5}$$

where n represents a particular PCB congener (n = 1 to 13; Table 3), and j is the injection or calibration solution number; (j = 1 to 5).

$$\overline{RF_{is}} = \frac{\sum_{j=1}^{5} RF_{is(j)}}{5}$$

where is represents a particular PCB internal standard (is = 14 to 23; Table 3), and j is the injection or calibration solution number; (j = 1 to 5).

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10.3 Operation Verification

At the beginning of each 12-hour shift during which analyses are performed, HRGC/HRMS system performance and calibration are verified for all native PCBs and labeled compounds. For these tests, analysis of the CS3 calibration verification (VER) standard (Section 7.5.6 and Table 4) and the isomer specificity test solution (Section 7.5.8 and Table 8) shall be used to verify all performance criteria. Adjustment and/or recalibration (Section 10) shall be performed until all performance criteria are met. Only after all performance criteria are met may samples and blanks be analyzed.

10.3.1 HRMS Resolution

A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at the appropriate m/z before any analysis is performed. Static resolving power checks must be performed at the beginning and at the end of each analysis batch according to procedures in Section 10.1.2. Corrective actions must be implemented whenever the resolving power does not meet the requirement.

10.3.2 Calibration Verification

10.3.2.1 Inject the VER standard using the procedure in Section 11.9.

10.3.2.2 The m/z abundance ratios for all PCBs shall be within the limits in Table 7; otherwise, the mass spectrometer shall be adjusted until the m/z abundance ratios fall within the limits specified, and the verification test shall be repeated. If the adjustment alters the resolution of the mass spectrometer, resolution shall be verified (Section 10.1.2) prior to repeat of the verification test.

10.3.2.3 The peaks representing each native PCB and labeled compound in the VER standard must be present with a S/N of at least 10; otherwise, the mass spectrometer shall be adjusted and the verification test repeated.

10.3.2.4 Calculate the relative response factors (RF) for unlabeled target analytes [$RF_{(n)}$; n = 1 to 13 from Table 3] relative to their appropriate internal standards (Table 2), and the RF_{is} for the $^{13}C_{12}$-labeled internal standards [$RF_{(is)}$; is = 14-23] relative to the recovery standards (Table 2) using the equations shown in Section 10.2.1.

10.3.2.5 For each compound, compare the relative response factor with those generated in the initial calibration. Relative response factors should be within 35 percent of initial calibration results for 70% of the analytes for the calibration to be verified. Once verified, analysis of standards and sample extracts may proceed. If, however, fewer than 70% of the response factors are within the 35% limit, the measurement system is

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not performing properly for those compounds. In this event, prepare a fresh calibration standard or correct the problem causing the failure and repeat the resolution (Section 10.1.2) and calibration verification (Section 10.3.2) tests, or recalibrate (Section 10). Per the analyst's discretion, results may also be reported for these analytes using the average calibration verification response factors bracketing the samples rather than the mean response factor generated in the initial calibration. If this option is chosen, data reported using an average calibration verification response factor should be flagged and discussed in the final report.

10.3.3 Retention Times

The absolute retention times of the GC/MS internal standards in the calibration verification shall be within ±15 seconds of the retention times obtained during initial calibration.

10.3.4 HRGC Resolution

10.3.4.1 Inject the GC retention time window defining and isomer specificity test solution (Section 7.5.8).

10.3.4.2 The valley height between PCBs 123 and 118 at m/z 325.8804 shall not exceed 25 percent, and the valley height between PCBs 156 and 157 shall not exceed 25 percent at m/z 359.8415 on the GC columns.

10.3.4.3 If the absolute retention time of any compound is not within the limits specified or if the congeners are not resolved, the GC is not performing properly. In this event, adjust the GC and repeat the calibration verification test or recalibrate, or replace the GC column and either verify calibration or recalibrate.

10.4 Data Storage

MS data shall be collected, recorded, and stored.

10.4.1 Data Acquisition

The signal at each exact m/z shall be collected repetitively throughout the monitoring period and stored on a mass storage device.

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10.4.2 Response Factors and Multipoint Calibrations

The data system shall be used to record and maintain lists of response factors and multipoint calibration curves. Computations of relative standard deviation (coefficient of variation) shall be used to test calibration linearity.

11.0 PROCEDURE

11.1 Sample preparation involves modifying the physical form of the sample so that the toxic PCBs can be extracted efficiently. For samples known or expected to contain high levels of the PCB analytes, the smallest sample size representative of the entire sample should be used. The method provides directions for samples that have either ≤5% solids or for samples that have >5% solids.

11.1.1 Scrubber water samples with 5% solids or less (visual estimate)

11.1.1.1 Shake or stir (with a clean glass rod) the sample for one minute to obtain a representative water aliquot. Transfer a 1-L aliquot to a clean bottle.

11.1.1.2 Spike the internal standard spiking solution (Section 7.5.3.2) into the bottle. Cap the bottle and mix the sample by shaking carefully. Allow the sample to equilibrate for 30 minutes, with occasional shaking.

11.1.1.3 Add 5 mL of methanol to the sample. Cap and shake the sample to mix thoroughly. Extract the sample using the SPE technique (Section 11.4.1), or an equivalent approved procedure.

11.1.2 Scrubber water with greater than 5% solids (visual estimate)

11.1.2.1 Determine percent solids according to Section 11.3.

11.1.2.2 Shake or stir (with a clean glass rod) the sample for one minute to obtain a representative water aliquot. Transfer a 1-L aliquot to a clean bottle.

11.1.2.3 Filter the aliquot and spike the filtrate with the internal standard spiking solution (Section 7.5.3.2). Allow the filtrate to equilibrate for 30 minutes with occasional shaking. Add 5 mL of methanol to the filtrate. Cap and shake the filtrate to mix thoroughly.

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11.1.2.4 Extract the filtrate using SPE as described in Section 11.4.1, or by using an equivalent approved procedure. Extract the filter and collected solids using Soxhlet techniques as described in Section 11.4.2.

11.2 Method Blank and Laboratory Spike Samples

11.2.1 With each sample set, a laboratory method blank and duplicate laboratory spike samples must be processed through the same steps as the samples to check for contamination and losses in the preparation processes.

11.2.2 For each sample or sample batch (to a maximum of 20 samples) to be extracted during the same 12-hour shift, place three 1.0-L aliquots of reagent water in clean sample bottles or flasks.

11.2.2.1 Spike two of these aliquots with PAR spiking solution (Section 7.5.7). These two PAR-spike aliquots will serve as the duplicate laboratory spike samples (Section 9.5).

11.2.2.2 The unspiked aliquot will serve as the laboratory method blank.

11.2.2.3 Process the duplicate laboratory spike samples and the laboratory method blank according to procedures for scrubber water with 5% solids or less (Section 11.1.1).

11.3 Percent Solids Determination

Note: This aliquot is used for determining the solids content of scrubber water samples with visually >5% solids content, and not for determination of PCBs.

11.3.1 Weigh a weighing pan or beaker to three significant figures.

11.3.2 Transfer 10.0 ± 0.02 g of well-mixed sample to the pan or beaker.

11.3.3 Dry the sample for a minimum of 12 hours at 110 ± 5°C and cool in a desiccator until the sample has equilibrated to room temperature. Weigh the dry sample plus beaker.

11.3.4 Calculate percent solids as follows:

$$\% \ solids = \frac{weight \ of \ sample \ plus \ beaker \ after \ drying \ (g) - weight \ of \ beaker \ (g)}{10 \ g} \times 100$$

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11.4 Extraction and Concentration

11.4.1 Extraction procedures include solid phase (Section 11.4.1) for scrubber water with a percent solids content of ≤5%.

11.4.2 A combination of solid phase (for the filtrate) and Soxhlet (for the solids) extraction procedures are provided for scrubber water with a percent solids content of >5%.

11.4.3 Solid Phase Extraction

11.4.3.1 SPE cartridge preparation

11.4.3.1.1 Place two SPE cartridges in the vacuum manifold.

11.4.3.1.2 Condition the cartridges with 15 mL aliquots of methylene chloride, methanol, and deionized water. Do not allow the cartridge to go dry from this point until the extraction is completed.

11.4.3.2 Sample extraction

11.4.3.2.1 Allow the sample to equilibrate for 1-2 hours to settle the suspended particles.

11.4.3.2.2 Allow a 1 L aliquot of the sample to be pulled through the two SPE cartridges (approximately 500 mL in each).

11.4.3.2.3 Adjust the vacuum to complete the extraction in no less than 15 minutes. An additional SPE cartridge may be used if clogging prevents sufficient sample throughput.

11.4.3.2.4 Before all of the sample has been pulled through the cartridge, add approximately 20 mL of reagent water to the sample bottle, swirl to suspend the solids (if present), and pour into the second reservoir. Pull through the SPE cartridge. Use additional reagent water rinses until all solids are removed.

11.4.3.2.5 Before all of the sample and rinses have been pulled through the cartridge, rinse the sides of the reservoir with small portions of reagent water.

11.4.3.2.6 Dry the cartridges under vacuum for 2 hours.

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11.4.3.3 Cartridge Elution

    11.4.3.3.1 Release the vacuum, remove reservoir from the vacuum manifold, and discard the extracted aqueous solution.

    11.4.3.3.2 Insert two vials for eluant collection into the manifold. Each vial should have sufficient capacity to contain the total volume of the elution solvent (approximately 12 mL) and should fit around the drip tip.

    11.4.3.3.3 The drip tip should protrude into the vial to preclude loss of sample from spattering when vacuum is applied. Reassemble the vacuum manifold.

    11.4.3.3.4 Wet each cartridge with 6 mL of acetone. Allow the solvent to soak the C_{18} beads for 15-20 seconds. Pull all of the solvent through the cartridges into the vials.

    11.4.3.3.5 Wet each cartridge with 6 mL of methylene chloride. Allow the solvent to soak the C_{18} beads for 15-20 seconds. Pull all of the solvent through the cartridge into the vial.

    11.4.3.3.6 Release the vacuum, remove the vial containing the sample solution.

    11.4.3.3.7 Quantitatively transfer the solution to a 250-mL separatory funnel (final volume is approximately 50 mL of hexane extract).

    11.4.3.3.8 If the percent solids content of the sample is ≤5%, proceed to Section 11.5 for acid and base partitioning.

    11.4.3.3.9 If the percent solids content of the sample is > 5%, combine the sample's filtrate extract with the solids extract, as specified in Section 11.4.2.10.

11.4.4 Soxhlet Extraction

    11.4.4.1 Place a clean extraction thimble (Section 6.3.3.2) in a clean extractor.

    11.4.4.2 Place 30 to 40 mL of methylene chloride in the receiver and 200 to 250 mL of methylene chloride in the flask.

    11.4.4.3 Load the solids and filter into the thimble.

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11.4.4.4 Add approximately 5 g of Na_2SO_4 to the thimble.

11.4.4.5 Add a plug of clean glass wool to the thimble to prevent the filter from floating on top of the extraction solvent.

11.4.4.6 Reassemble the Soxhlet apparatus, and apply power to the heating mantle to begin extracting. Frequently check the apparatus for foaming during the first 2 hours of extraction. If foaming occurs, reduce the extraction rate until foaming subsides.

11.4.4.7 Extract the solids/filter for a total of 16 to 24 hours. Cool and disassemble the apparatus.

11.4.4.8 Concentrate the extract to a final volume of 10 mL; transfer 5 mL of the extract to a 10 mL storage vial with a PTFE-lined screw cap. Label the extract and store at $<0°C$. Mark the liquid level on the vial with a permanent marker to monitor solvent evaporation during storage.

11.4.4.9 Solvent exchange the other half of the extract (5 mL) into hexane by adding 10 mL of hexane, concentrating down to 1 mL using K-D evaporation, adding 10 mL hexane, and concentrating down again to 2 mL. Transfer the extract with three aliquots (15 mL each) of hexane into a 250-mL separatory funnel. Proceed to Section 11.5 to start cleanup procedures.

11.4.4.10 Combine the water filtrate extract from Section 11.4.3.3.9 with the solids extract. Proceed to Section 11.5 to begin the cleanup procedure.

11.5 Acid and Base Partitioning

11.5.1 Spike the cleanup standard (Section 7.5.4) into the separatory funnels containing the sample extracts from Section 11.4.

11.5.2 Partition the extract against 50 mL of sulfuric acid (Section 7.1.2). Shake for 2 minutes with periodic venting into a hood. Remove and discard the aqueous layer. Repeat the acid washing until no color is visible in the aqueous layer to a maximum of four washings.

11.5.3 Partition the extract against 50 mL of sodium chloride solution (Section 7.1.4) in the same way as with the acid. Discard the aqueous layer.

11.5.4 Partition the extract against 50 mL of potassium hydroxide solution (Section 7.1.1) in the same way as with the acid. Repeat the base washing until

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no color is visible in the aqueous layer to a maximum of four washings. Minimize contact time between the extract and the base to prevent degradation of the PCBs.

11.5.5 Repeat the partitioning against sodium chloride solution two more times, each time discarding the aqueous layer.

11.5.6 Pour each extract through a drying column containing 7 to 10 cm of granular anhydrous sodium sulfate (Section 7.2.1). Rinse the separatory funnel with 30 to 50 mL of solvent, and pour through the drying column. Collect each extract in a round-bottom flask.

11.5.7 Concentrate the extracts (Sections 11.6), and clean the extracts per Section 11.7.

11.6 Macro-Concentration – Extracts in methylene chloride or n-hexane are concentrated using rotary evaporation, a Kuderna-Danish, or Turbovap apparatus.

11.6.1 Rotary evaporation – Concentrate the extracts in separate round-bottom flasks.

Note: Improper use of the rotary evaporator may cause contamination of the sample extract.

11.6.1.1 Assemble the rotary evaporator according to manufacturer's instructions, and warm the water bath to 45°C. On a daily basis, preclean the rotary evaporator by concentrating 100 mL of clean extraction solvent through the system. Archive both the concentrated solvent and the solvent in the catch flask for a contamination check if necessary. Between samples, use three 2- to 3-mL aliquots of solvent to rinse the feed tube between samples. Collect waste in a waste beaker.

11.6.1.2 Attach the round-bottom flask containing the sample extract to the rotary evaporator. Slowly apply vacuum to the system, and begin rotating the sample flask.

11.6.1.3 Lower the flask into the water bath, and adjust the speed of rotation and the temperature as required to complete concentration in 15 to 20 minutes. At the proper rate of concentration, the flow of solvent into the receiving flask must be steady, with no bumping or visible boiling of the extract occurring.

Note: If the rate of concentration is too fast, analyte loss may occur.

11.6.1.4 When the liquid in the concentration flask has reached an apparent volume of approximately 2 mL, remove the flask from the water bath

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and stop the rotation. Slowly and carefully admit air into the system. Be sure not to open the valve so quickly that the sample is blown out of the flask. Rinse the feed tube with approximately 2 mL of solvent.

11.6.2 Kuderna-Danish (K-D)—Concentrate the extracts in separate 500-mL K-D flasks equipped with 10-mL concentrator tubes. The K-D technique is used for solvents such as methylene chloride and n-hexane.

11.6.2.1 Add 1 to 2 clean boiling chips to the receiver. Attach a three-ball macro-Snyder column. Pre-wet the column by adding approximately 1 mL of solvent through the top. Place the K-D apparatus in a hot water bath so that the entire lower rounded surface of the flask is bathed with steam.

11.6.2.2 Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

11.6.2.3 When the liquid has reached an apparent volume of 1 mL, remove the K-D apparatus from the bath and allow the solvent to drain and cool for at least 10 minutes.

11.6.2.4 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of solvent. A 5-mL syringe is recommended for this operation.

11.6.2.5 Remove the three-ball Snyder column, add a fresh boiling chip, and attach a two-ball micro-Snyder column to the concentrator tube. Pre-wet the column by adding approximately 0.5 mL of solvent through the top. Place the apparatus in the hot water bath.

11.6.2.6 Adjust the vertical position and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

11.6.2.7 When the liquid reaches an apparent volume of 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes.

11.6.3 Turbovap – Concentrate the extracts in separate 250-mL Turbotubes. The Turbovap technique is used for solvents such as methylene chloride and n-hexane.

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11.7 Column Chromatography Cleanup

11.7.1 Silica Gel Cleanup

11.7.1.1 Place a glass-wool plug in a 15-mm ID chromatography column (Section 6.5.2.2). Pack the column bottom to top with 1 g silica gel (Section 7.4.1.1), 4 g basic silica gel (Section 7.4.1.3), 1 g silica gel, 8 g acid silica gel (Section 7.4.1.2), 2 g silica gel, and 4 g granular anhydrous sodium sulfate (Section 7.2.1). Tap the column to settle the adsorbents.

11.7.1.2 Pre-elute the column with 50 to 100 mL of n-hexane. Close the stopcock when the n-hexane is within 1 mm of the sodium sulfate. Discard the eluate. Check the column for channeling. If channeling is present, discard the column and prepare another.

11.7.1.3 Apply the concentrated extract to the column. Open the stopcock until the extract is within 1 mm of the sodium sulfate.

11.7.1.4 Rinse the receiver twice with 1-mL portions of n-hexane, and apply separately to the column. Elute the PCBs with 75 mL of n-hexane and collect the eluate.

11.7.1.5 Concentrate the eluate per Section 11.6 and proceed to Section 11.8.2 for carbon column cleanup.

11.7.1.6 For extracts of samples known to contain large quantities of other organic compounds, it may be advisable to increase the capacity of the silica gel column. This may be accomplished by increasing the strengths of the acid and basic silica gels. The acid silica gel (Section 7.4.1.2) may be increased in strength to as much as 44% w/w (7.9 g sulfuric acid added to 10 g silica gel). The basic silica gel (Section 7.4.1.3) may be increased in strength to as much as 33% w/w (50 mL 1N NaOH added to 100 g silica gel).

11.7.2 Carbon Column

11.7.2.1 Cut both ends from a 50-mL disposable serological pipet (Section 6.6.1.2) to produce a 20-cm column. Fire-polish both ends and flare both ends if desired. Insert a glass-wool plug at one end, and pack the column with 3.6 g of Carbopak/Celite (Section 7.4.2.3) to form an adsorbent bed 20 cm long. Insert a glass-wool plug on top of the bed to hold the adsorbent in place.

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11.7.2.2 Pre-elute the column with 20 mL each in succession of methylene chloride, and n-hexane.

11.7.2.3 When the solvent is within 1 mm of the column packing, apply the n-hexane sample extract to the column. Rinse the sample container twice with 1-mL portions of n-hexane and apply separately to the column. Apply 2 mL of n-hexane to complete the transfer.

11.7.2.4 Elute the column with 25 mL of n-hexane and collect the eluate. This fraction will contain the mono- and di-ortho PCBs.

11.7.2.5 Elute the column with 15 mL of methanol and archive the eluate. This second fraction will contain residual lipids and other potential interferents, if present.

11.7.2.6 Elute the column with 15 mL of toluene and collect the eluate. This fraction will contain PCBs 77, 126, and 169. Combine the first and third fractions, and if carbon particles are present in the combined eluate, filter through glass-fiber filter paper.

11.7.2.7 Concentrate the combined hexane and toluene fractions per Section 11.6 and proceed to Section 11.8 for final concentration.

11.8 Concentration to Final Volume

11.8.1 The extract is concentrated in a calibrated concentrator tube to a final volume of 20 μL to 1 mL, per the analyst's discretion, under a gentle stream of nitrogen.

11.8.2 Add 10 µL of the recovery standard solution (Section 7.5.5) to the sample extract.

11.8.3 Proceed to Section 11.9 for HRGC/HRMS analysis.

11.9 HRGC/HRMS Analysis

11.9.1 Establish the operating conditions given in Section 10.1, perform initial calibration if necessary (Section 10.2), or verify calibration (Section 10.3).

11.9.2 If an extract is to be reanalyzed and evaporation has occurred, do not add more recovery standard solution. Instead, bring the extract back to its previous volume (e.g., 19 µL, or 18 µL if 2 µL injections are used) with pure nonane.

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11.9.3 Inject 1.0 or 2.0 μL of the concentrated extract containing the recovery standard solution, using on-column or splitless injection. The volume injected must be identical to the volume used for calibration (Section 10.1.3.1).

11.9.4 Start the HRGC column initial isothermal hold upon injection. Start HRGMS data collection after the solvent peak elutes. Stop the data collection after the $^{13}C_{12}$-PCB 209 has eluted. Return the column to the initial temperature for analysis of the next extract or standard.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Qualitative Determination

A PCB analyte or labeled compound is identified in a standard, blank, or sample when all of the criteria in Sections 12.1.1 through 12.1.4 are met. If the criteria for identification in Sections 12.1.1-12.1.4 are not met, the PCB analyte has not been positively identified. If interferences preclude identification, an estimated maximum possible concentration (EMPC) can be reported (Section 12.2.5), or options for further cleanup can be explored depending on specific project requirements.

12.1.1 The signals for the two exact m/z's in Table 6 must be present and must maximize within the same two seconds.

12.1.2 The signal-to-noise ratio (S/N) for the GC peak at each exact m/z must be greater than or equal to 2.5 for each PCB detected in a sample extract and greater than or equal to 10 for all PCBs in the calibration standard (Section 7.5.6).

12.1.3 The ratio of the integrated areas of the two exact m/z's specified in Table 6 must be within the limit in Table 7, or within ±10 percent of the ratio in the midpoint (CS3) calibration or calibration verification (VER) whichever is most recent.

12.1.4 The relative retention time of the peak for a toxic PCB must be within ±15 seconds of the retention times obtained during calibration.

12.2 Quantitative Determination

12.2.1 For gas chromatographic peaks that have met the criteria outlined in Section 12.1, calculate the concentration of the PCB compounds in the extract, using the formula:

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$$C_x = \frac{A_x \times Q_{is}}{A_{is} \times \overline{RF}_n \times V_s}$$

where:

C_x = *concentration of unlabeled PCB congeners in the sample (pg/L),*

A_x = *sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and 6) for unlabeled PCBs,*

A_{is} = *sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and 6) for the labeled internal standards,*

$\underline{Q_{is}}$ = *quantity, in pg, of the internal standard added to the sample before extraction,*

$\overline{RF}_n$ = *calculated mean relative response factor for the analyte (RF_n with n=1 to 13; Section 10.2.1),*

V_s = *volume of sample extracted (L).*

12.2.2   Calculate the percent recovery of the eleven internal standards measured in the sample extract, using the formula:

$$Percent\ recovery = \frac{A_{is} \times Q_{rs}}{Q_{is} \times A_{rs} \times \overline{RF}_{is}} \times 100$$

where:

A_{is} = *sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and 6) for the labeled internal standard,*

A_{rs} = *sum of the integrated ion abundances of the quantitation ions (Tables 2, 3 and 6) for the labeled recovery standard,*

Q_{is} = *quantity, in ng, of the internal standard added to the sample before extraction,*

Q_{rs} = *quantity, in ng, of the recovery standard added to the cleaned-up sample extract before HRGC/HRMS analysis, and*

$\overline{RF}_{is}$ = *calculated mean relative response factor for the labeled internal standard relative to the appropriate recovery standard. This represents the mean obtained in Section 10.2.2 ($\overline{RF}_{is}$ with is = 14 to 23, Table 3).*

The percent recovery of the cleanup standards is calculated similarly. The percent recovery should meet the criteria shown in Table 5. If recoveries are outside the limits of Table 5, the data should be flagged and the impact on reported results discussed in the final report.

12.2.3   Outside Calibration Range

12.2.3.1   If the SICP area at either quantitation m/z for any compound exceeds the calibration range of the system, the extract must be diluted and re-analyzed.

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12.2.3.2   Dilute the sample extract by a factor of 10, adjust the concentration of the recovery standard to 100 pg/μL in the extract, and analyze an aliquot of this diluted extract.

12.2.4   Estimated Detection Limit (EDL)

$$EDL \ (pg \ / \ L) = \frac{2.5 \ (H1_s + H2_s) \ (Q_{is})}{(H1_{is} + H2_{is}) \ (\overline{RF_n}) \ (V_s)}$$

where:

$H1_s$ and $H2_s$ = *The heights of the noise where the primary and secondary m/z's for the PCBs would elute.*

$H1_{is}$ and $H2_{is}$ = *The heights of the response of the primary and secondary m/z's for the internal standard,*

And Q_{is}, $\overline{RF_n}$, and V_s are as described in Section 12.2.1.

12.2.5   Estimated Maximum Possible Concentration (EMPC)

When the response of a signal having the same retention time as a toxic PCB congener has a S/N in excess of 2.5 and does not meet all of the other qualitative identification criteria listed in Section 12.1 calculate an Estimated Maximum Possible Concentration (EMPC). The EMPC is calculated using the equation in Section 12.2.1, except that A_x should represent the sum of the area under the smaller peak and of the other peak area calculated using the theoretical chlorine isotope ratio. The value shall be noted as EMPC and the results reported.

12.2.6   Results are reported to three significant figures for the PCBs and labeled compounds found in all standards, blanks, and samples.

Note: Reported results will not be adjusted for field or laboratory blank levels.

12.2.6.1   Scrubber Water— results in pg/L (parts-per-quadrillion).

12.2.6.2   Blanks—Report results above the EDL. Do not blank-correct results. If a blank accompanying a sample result shows contamination above the EDL for the congener, flag the sample result and report the results for the sample and the accompanying blank.

12.2.6.3   Dilutions (Section 12.2.3.2)

Results for PCB analytes in samples that have been diluted; for this EPA project, both the undiluted and diluted PCB results are to be

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reported, whether or not all of the analytes are within the calibration range.

12.2.7.4   Non-Detects

Note the non-detected PCB analytes as ND and report the estimated detection limit established during the analysis.

13.0 METHOD PERFORMANCE

13.1   In a limited single laboratory demonstration of this method using scrubber water samples, estimated detection limits of approximately 25 pg/L were achieved for PeCB; 5 pg/L for HxCB; and 30 pg/L for HpCB.

13.2   Interlaboratory testing of this method to determine overall precision and bias has not been performed.

14.0 POLLUTION PREVENTION

This method uses solid phase extraction (SPE) techniques for the extraction of PCBs from liquid matrices. SPE uses much less solvent, about 1/100 as much, as traditional liquid-liquid extraction techniques.

15.0 WASTE MANAGEMENT

PCB waste should be disposed of according to Toxic Substances Control Act (TSCA) guidelines 40CFR 700-789, and hazardous waste should be disposed of according to Resource Conservation and Recovery Act (RCRA) guidelines 40CFR 260-269.

16.0 REFERENCES

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17.0   TABLES AND FIGURES

Table 1. Toxic Polychlorinated Biphenyls Determined by High Resolution Gas Chromatography (HRGC)/High Resolution Mass Spectrometry (HRMS)

PCB[1]	Native compound CAS Registry No.	IUPAC No.[2]
Target Analytes		
3,3',4,4'-TCB	32598-13-3	77
2,3,3',4,4'-PeCB	32598-14-4	105
2,3,4,4',5-PeCB	74472-37-0	114
2,3',4,4',5-PeCB	31508-00-6	118
2',3,4,4',5-PeCB	65510-44-3	123
3,3',4,4',5-PeCB	57465-28-8	126
2,3,3',4,4',5-HxCB	38380-08-4	156
2,3,3',4,4',5'-HxCB	69782-90-7	157
2,3',4,4',5,5'-HxCB	52663-72-6	167
3,3',4,4',5,5'-HxCB	32774-16-6	169
2,2',3,3',4,4',5-HpCB	35065-30-6	170
2,2',3,4,4',5,5'-HpCB	35065-29-3	180
2,3,3',4,4',5,5'-HpCB	39635-31-9	189
Internal Standards		
3,3',4,4'-TCB	160901-67-7	77L
2,3,3',4,4'-PeCB	160901-70-2	105L
2,3,4,4',5-PeCB	160901-72-4	114L
2,3',4,4',5-PeCB	160901-73-5	118L
2',3,4,4',5-PeCB	160901-74-6	123L
3,3',4,4',5-PeCB	160901-75-7	126L
2,3,3',4,4',5-HxCB	160901-77-9	156L
2,3,3',4,4',5'-HxCB	160901-78-0	157L
2,3',4,4',5,5'-HxCB	161627-18-5	167L
3,3',4,4',5,5'-HxCB	160901-79-1	169L
2,2',3,3',4,4',5-HpCB	160901-80-4	170L
2,2',3,4,4',5,5'-HpCB	160901-82-6	180L
2,3,3',4,4',5,5'-HpCB	160901-83-7	189L
Cleanup Standards		
$^{13}C_{12}$-3,4,4',5-TCB	160901-68-8	81
$^{13}C_{12}$-2,3,3',5,5'-PeCB	160901-71-3	111
Recovery Standards		
$^{13}C_{12}$-2,2',5,5'-TCB	160901-66-6	52
$^{13}C_{12}$-2,2',4,4,5'-PeCB	160901-69-9	101
$^{13}C_{12}$-2,2',3,4,4',5'-HxCB	160901-76-8	138
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB	160901-81-5	178
Final Eluter Standard		
$^{13}C_{12}$-DCB	160901-84-8	209

[1] Polychlorinated biphenyls:
    TCB = Tetrachlorobiphenyl
    PeCB = Pentachlorobiphenyl
    HxCB = Hexachlorobiphenyl
    HpCB = Heptachlorobiphenyl
    DCB = Decachlorobiphenyl

[2] Suffix "L" designates a labeled compound.

Table 2. Retention Time (RT) References, Quantitation References, and Retention Times (RTs) for the Toxic PCBs

IUPAC No.[1]	PCB congener	IUPAC No.[1]	Retention time and quantitation reference	RT[2] (min)
52L	13C12-2,2',5,5'-TCB	—[3]	13C12-2,2',5,5'-TCB	28.56
81L	13C12-3,4,4',5-TCB[4]	52L	13C12-2,2',5,5'-TCB	37.89
77L	13C12-3,3',4,4'-TCB	52L	13C12-2,2',5,5'-TCB	38.85
77	3,3',4,4'-TCB	77L	13C12-3,3',4,4'-TCB	38.85
101L	13C12-2,2',4,5,5'-PeCB	—	13C12-2,2',4,5,5'-PeCB	35.02
111L	13C12-2,3,3',5,5'-PeCB[4]	101L	13C12-2,2',4,5,5'-PeCB	37.13
123	2',3,4,4',5-PeCB	118L	13C12-2,3',4,4',5-PeCB	39.90
118L	13C12-2,3',4,4',5-PeCB	101L	13C12-2,2',4,5,5'-PeCB	40.17
118	2,3',4,4',5-PeCB	118L	13C12-2,3',4,4',5-PeCB	40.17
114	2,3,4,4',5-PeCB	105L	13C12-2,3,3',4,4'-PeCB	40.79
105L	13C12-2,3,3',4,4'-PeCB	101L	13C12-2,2',4,5,5'-PeCB	42.22
105	2,3,3',4,4'-PeCB	105L	13C12-2,3,3',4,4'-PeCB	42.22
126L	13C12-3,3',4,4',5-PeCB	101L	13C12-2,2',4,5,5'-PeCB	44.75
126	3,3',4,4',5-PeCB	126L	13C12-3,3',4,4',5-PeCB	44.75
138L	13C12-2,2',3,4,4',5'-HxCB	—	13C12-2,2',4,5,5'-PeCB	43.23
167L	13C12-2,3',4,4',5,5'-HxCB	138L	13C12-2,2',3,4,4',5'-HxCB	45.72
167	2,3',4,4',5,5'-HxCB	167L	13C12-2,3',4,4',5,5'-HxCB	45.72
156L	13C12-2,3,3',4,4',5-HxCB	138L	13C12-2,2',3,4,4',5'-HxCB	47.37
157L	13C12-2,3,3',4,4',5'-HxCB	138L	13C12-2,2',3,4,4',5'-HxCB	47.79
156	2,3,3',4,4',5-HxCB	156L	13C12-2,3,3',4,4',5-HxCB	47.37
157	2,3,3',4,4',5'-HxCB	157L	13C12-2,3,3',4,4',5'-HxCB	47.79
169L	13C12-3,3',4,4',5,5'-HxCB	138L	13C12-2,2',3,4,4',5'-HxCB	50.25
169	3,3',4,4',5,5'-HxCB	169L	13C12-3,3',4,4',5,5'-HxCB	50.25
178L	13C12-2,2',3,3',5,5',6-HpCB	—	13C12-2,2',4,5,5'-PeCB	42.88
180L	13C12-2,2',3,4,4',5,5'-HpCB	178L	13C12-2,2',3,3',5,5',6-HpCB	47.88
180	2,2',3,4,4',5,5'-HpCB	180L	13C12-2,2',3,4,4',5,5'-HpCB	47.88
170	2,2',3,3',4,4',5-HpCB	180L	13C12-2,2',3,4,4',5,5'-HpCB	49.90
189L	13C12-2,3,3',4,4',5,5'-HpCB	178L	13C12-2,2',3,3',5,5',6-HpCB	52.56
189	2,3,3',4,4',5,5'-HpCB	189L	13C12-2,3,3',4,4',5,5'-HpCB	52.56
209L	13C12-DCB[5]	178L	13C12-2,2',3,3',5,5',6-HpCB	56.63

[1] Suffix "L" indicates labeled compound.
[2] Retention time data are for HT-8 column (per manufacturer).
[3] Absolute recovery standards.
[4] Cleanup standard.
[5] Final eluter.

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Table 3. Concentrations of Stock and Spiking Solutions Containing the Native PCBs and Labeled Compounds

Cpd. No.	Compound	m/z type	Stock[3] (ng/mL)	Spiking Solution[2] (ng/mL)	Spiking Level (ng)
	Precision and Recovery Standards[1]				
1	3,3',4,4'-TCB	77	20	0.8	0.8
2	2,3,3',4,4'-PeCB	105	1000	40	40
3	2,3,4,4',5-PeCB	114	1000	40	40
4	2,3',4,4',5-PeCB	118	1000	40	40
5	2',3,4,4',5-PeCB	123	1000	40	40
6	3,3',4,4',5-PeCB	126	100	4	4
7	2,3,3',4,4',5-HxCB	156	1000	40	40
8	2,3,3',4,4',5'-HxCB	157	1000	40	40
9	2,3',4,4',5,5'-HxCB	167	1000	40	40
10	3,3',4,4',5,5'-HxCB	169	200	8	8
11	2,2',3,3',4,4',5-HpCB	170	200	8	8
12	2,2',3,4,4',5,5'-HpCB	180	1000	40	40
13	2,3,3',4,4',5,5'-HpCB	189	200	8	8
	Internal Standards[4]				
14	13C12-3,3',4,4'-TCB	77L	1000	4	4
15	13C12-2,3,3',4,4'-PeCB	105L	1000	4	4
16	13C12-2,3',4,4',5-PeCB	118L	1000	4	4
17	13C12-3,3',4,4',5-PeCB	126L	1000	4	4
18	13C12-2,3,3',4,4',5-HxCB	156L	1000	4	4
19	13C12-2,3,3',4,4',5'-HxCB	157L	1000	4	4
20	13C12-2,3',4,4',5,5'-HxCB	167L	1000	4	4
21	13C12-3,3',4,4',5,5'-HxCB	169L	1000	4	4
22	13C12-2,2',3,4,4',5,5'-HpCB	180L	1000	4	4
23	13C12-2,3,3',4,4',5,5'-HpCB	189L	1000	4	4
	Cleanup Standards[5]				
24	13C12-3,4,4',5-TCB	81L	200	1	1
25	13C12-2,3,3',5,5'-PeCB	111L	1000	5	5
	Recovery Standards[6]				
26	13C12-2,2',5,5'-TCB	52L	1000	200	2
27	13C12-2,2',4,5,5'-PeCB	101L	1000	200	2
28	13C12-2,2',3,4,4',5'-HxCB	138L	1000	200	2
29	13C12-2,2',3,3',5,5',6-HpCB	178L	1000	200	2
	Final Eluter				
30	13C12-DCB	209L	2000	8	8

[1] Section 7.5.7-prepared in nonane and diluted to prepare spiking solution.

[2] Sections 7.5.3.2, 7 5.4., 7.5.5, 7.5.7-prepared in acetone from stock solution daily.

[3] Section 7.5.1-prepared in nonane and diluted to prepare spiking solution. Concentrations are adjusted for expected background levels.

[*] Section 7.5.3.2-prepared in acetone from stock solution daily. Concentrations are adjusted for expected background levels.

[5] Section 7.5.4-prepared in acetone; added to sample extracts before cleanup.

[6] Section 7.5.5-prepared in nonane; added to concentrated extract prior to injection.

Table 4. Concentrations of PCBs in Calibration and Calibration Verification Solutions

	IUPAC No.[1]	CS1 (ng/mL)	CS2 (ng/mL)	CS3[2] (ng/mL)	CS4 (ng/mL)	CS5 (ng/mL)
Precision and Recovery Standards						
3,3',4,4'-TCB	77	0.5	2	10	40	200
2,3,3',4,4'-PeCB	105	2.5	10	50	200	1000
2,3,4,4',5-PeCB	114	2.5	10	50	200	1000
2,3',4,4',5-PeCB	118	2.5	10	50	200	1000
2',3,4,4',5-PeCB	123	2.5	10	50	200	1000
3,3',4,4',5-PeCB	126	2.5	10	50	200	1000
2,3,3',4,4',5-HxCB	156	5	20	100	400	2000
2,3,3',4,4',5'-HxCB	157	5	20	100	400	2000
2,3',4,4',5,5'-HxCB	167	5	20	100	400	2000
3,3',4,4',5,5'-HxCB	169	5	20	100	400	2000
2,2',3,3',4,4',5-HpCB	170	5	20	100	400	2000
2,2',3,4,4',5,5'-HpCB	180	5	20	100	400	2000
2,3,3',4,4',5,5'-HpCB	189	5	20	100	400	2000
Internal Standards						
13C12-3,3',4,4'-TCB	77L	100	100	100	100	100
13C12-2,3,3',4,4'-PeCB	105L	100	100	100	100	100
13C12-2,3',4,4',5-PeCB	118L	100	100	100	100	100
13C12-3,3',4,4',5-PeCB	126L	100	100	100	100	100
13C12-2,3,3',4,4',5-HxCB	156L	100	100	100	100	100
13C12-2,3,3',4,4',5'-HxCB	157L	100	100	100	100	100
13C12-2,3',4,4',5,5'-HxCB	167L	100	100	100	100	100
13C12-3,3',4,4',5,5'-HxCB	169L	100	100	100	100	100
13C12-2,2',3,4,4',5,5'-HpCB	180L	100	100	100	100	100
13C12-2,3,3',4,4',5,5'-HpCB	189L	100	100	100	100	100
Cleanup Standards						
13C12-3,4,4',5-TCB	81L	0.5	2	10	40	200
13C12-2,3,3',5,5'-PeCB	111L	2.5	10	50	200	1000
Recovery Standards						
13C12-2,2',5,5'-TCB	52L	100	100	100	100	100
13C12-2,2',4,5,5'-PeCB	101L	100	100	100	100	100
13C12-2,2',3,4,4',5'-HxCB	138L	100	100	100	100	100
13C12-2,2',3,3',5,5',6-HpCB	178L	100	100	100	100	100
Final Eluter						
13C12-DCB	209L	200	200	200	200	200

[1] Suffix "L" indicates labeled compound.
[2] Sections 7.5.6, calibration verification solution.

Table 5. Target Labeled Compound Recovery in Samples

Labeled PCB	IUPAC No.	Test conc $(ng/mL)^1$	Labeled compound recovery (ng/mL)	(%)
Internal Standards				
13C12-3,3',4,4'-TCB	77	100	20-160	20-160
13C12-2,3,3',4,4'-PeCB	105	100	20-160	20-160
13C12-2,3',4,4',5-PeCB	118	100	20-160	20-160
13C12-3,3',4,4',5-PeCB	126	100	20-160	20-160
13C12-2,3,3',4,4',5-HxCB	156	100	20-160	20-160
13C12-2,3,3',4,4',5'-HxCB	157	100	20-160	20-160
13C12-2,3',4,4',5,5'-HxCB	167	100	20-160	20-160
13C12-3,3',4,4',5,5'-HxCB	169	100	20-160	20-160
13C12-2,2',3,4,4',5,5'-HpCB	180	100	20-160	20-160
13C12-2,3,3',4,4',5,5'-HpCB	189	100	20-160	20-160
Cleanup Standards		--		
13C12-3,4,4',5-TCB	81	50	4-32	20-160
13C12-2,3,3',5,5'-PeCB	111	250	40-140	40-140

^{1} Based on 20 μL final extract volume.

Table 6. Descriptors, Exact m/z's, m/z Types, and Elemental Compositions of the PCBs

Descriptor	Exact m/z[1]	m/z type	Elemental composition	Substance[2]
1.	289.9224	M	C12 H6 35Cl4	TCB
	291.9194	M+2	C12 H6 35Cl3 37Cl	TCB
	301.9626	M	13C12 H6 35Cl4	TCB[3]
	303.9597	M+2	13C12 H6 35Cl3 37Cl	TCB[3]
	318.9792	Lock Mass	--	PFK
	325.8804	M+2	C12 H5 35Cl4 37Cl	PeCB
	327.8775	M+4	C12 H5 35Cl3 37Cl2	PeCB
	330.9793	Lock Mass Check	--	PFK
	337.9207	M+2	13C12 H5 35Cl4 37Cl	PeCB[3]
	339.9178	M+4	13C12 H5 35Cl3 37Cl2	PeCB[3]
2.	325.8804	M+2	C12 H5 35Cl4 37Cl	PeCB
	327.8775	M+4	C12 H5 35Cl3 37Cl2	PeCB
	337.9207	M+2	13C12 H5 35Cl4 37Cl	PeCB[3]
	339.9178	M+4	13C12 H5 35Cl3 37Cl2	PeCB[3]
	354.9792	Lock Mass	--	PFK
	354.9792	Lock Mass Check	--	PFK
	393.8025	M+2	C12 H3 35Cl6 37Cl	HpCB
	395.7996	M+4	C12 H3 35Cl5 37Cl2	HpCB
	405.8428	M+2	13C12 H3 35Cl6 37Cl	HpCB[3]
	407.8398	M+4	13C12 H3 35Cl5 37Cl2	HpCB[3]
3.	359.8415	M+2	C12 H4 35Cl5 37Cl	HxCB
	361.8385	M+4	C12 H4 35Cl4 37Cl2	HxCB
	371.8817	M+2	13C12 H4 35Cl5 37Cl	HxCB[3]
	373.8788	M+4	13C12 H4 35Cl4 37Cl2	HxCB[3]
	380.9760	Lock Mass	--	PFK
	380.9760	Lock Mass Check	--	PFK
	393.8025	M+2	C12 H3 35Cl6 37Cl	HpCB
	395.7996	M+4	C12 H3 35Cl5 37Cl2	HpCB
	405.8428	M+2	13C12 H3 35Cl6 37Cl	HpCB[3]
	407.8398	M+4	13C12 H3 35Cl5 37Cl2	HpCB[3]
4.	504.9696	Lock Mass	--	PFK
	504.9696	Lock Mass Check	--	PFK
	509.7229	M+4	13C12 35Cl8 37Cl2	DCB[3]
	511.7199	M+6	13C12 35Cl7 37Cl3	DCB[3]

[1] Nuclidic masses used were:
    H = 1.007825   C = 12.00000
    13C = 13.003355   35Cl = 34.968853   37Cl = 36.965903
[2] TCB = Tetrachlorobiphenyl
   PeCB = Pentachlorobiphenyl
   HxCB = Hexachlorobiphenyl
   HpCB = Heptachlorobiphenyl
   DCB = Decachlorobiphenyl.
[3] 13C labeled compound.

Table 7. Theoretical Ion Abundance Ratios and QC Limits

Chlorine atoms	m/z's forming ratio	Theoretical ratio	QC Limit[1]	
			Lower	Upper
4	M/(M+2)	0.77	0.65	0.89
5	(M+2)/(M+4)	1.55	1.32	1.78
6	(M+2)/(M+4)	1.24	1.05	1.43
7	(M+2)/(M+4)	1.05	0.88	1.20
10	(M+4)/(M+6)	1.17	0.99	1.35

[1] QC limits represent +/- 15 percent windows around the theoretical ion abundance ratio. These limits are preliminary.

Table 8. GC Retention Time Window Defining and Congener Specificity Test Solution[1]
(Section 7.5.8)

Congener group	First eluted		Last eluted	
TCB	54	2,2',6,6'	77	3,3',4,4'
PeCB	104	2,2',4,6,6'	126	3.3',4,4',5
HxCB	155	2,2',4,4',6,6'	169	3,3',4,4',5,5'
HpCB	188	2,2',3,4',5,6,6'	189	2,3,3',4,4',5,5'

Isomer specificity test compounds

123	2',3,4,4',5-PeCB	156	2,3,3',4,4',5-HxCB	
118	2,3',4,4',5-PeCB	157	2,3,3',4,4',5'-HxCB	

[1] All compounds are at a concentration of 100 ng/mL in nonane.

```
                    ┌─────────────────────────┐
                    │  Scrubber Water Sample  │
                    └─────────────────────────┘
                                 │
                                 ▼
                    ┌─────────────────────────┐
                    │ Visually Estimate Percent│
                    │ Solids Content of Sample │
                    └─────────────────────────┘
                          ╱            ╲
                         ╱              ╲
        ┌──────────────────────┐   ┌──────────────────────┐
        │ Samples with <= 5% Solids│ │ Samples with > 5% Solids│
        └──────────────────────┘   └──────────────────────┘
                    │                         │
                    ▼                         ▼
        ┌──────────────────────┐   ┌──────────────────────┐
        │ Spike 1 L of Sample with│ │  Filter 1 L of Sample │
        │ Labeled Internal Standards│└──────────────────────┘
        └──────────────────────┘       ╱            ╲
                    │                  ╱              ╲
                    ▼        ┌──────────────┐  ┌──────────────┐
        ┌──────────────────┐ │ Spike Liquid │  │ Extract the  │
        │ Extract Using SPE│ │ with Labeled │  │ Solids using │
        └──────────────────┘ │  Internal    │  │  Soxhlet     │
                    │        │  Standards   │  │  Technique   │
                    │        └──────────────┘  └──────────────┘
                    │               │                 │
                    │               ▼                 │
                    │        ┌──────────────┐         │
                    │        │ Extract the  │         │
                    │        │ Liquid Filtrate│       │
                    │        │  Using SPE   │         │
                    │        └──────────────┘         │
                    │               │                 │
                    │               ▼                 │
                    │    ┌─────────────────────────┐  │
                    │    │ Combine Extracts from the│◄─┘
                    │    │ Solids and Liquid Sample │
                    │    └─────────────────────────┘
                    │               │
                    │               ▼
                    │    ┌──────────────────────┐  ┌──────────────┐
                    └───►│ Concentrate Extract to 10 mL│►│ Archive 5 mL │
                         └──────────────────────┘  └──────────────┘
                                    │
                                    ▼
                         ┌──────────────────────┐
                         │ Solvent Exchange 5 mL of│
                         │ Sample Extract to Hexane (50│
                         │         mL)          │
                         └──────────────────────┘
                                    │
                                    ▼
                         ┌──────────────────────┐
                         │ Spike with Cleanup Standard│
                         └──────────────────────┘
                                    │
                                    ▼
                         ┌──────────────────────┐
                         │ Proceed to Sample Cleanup│
                         │ Flow Diagram (Figure 2) │
                         └──────────────────────┘
```

Figure 1. Extraction Procedure for Scrubber Water Sample

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```
┌─────────────────────┐
│   See Figure 1 for  │
│   Description of     │
│  Sample Extraction  │
└─────────────────────┘
           │
           ▼
┌─────────────────────┐
│  Extract Hexane Extract │
│  with Sulfuric Acid*    │
└─────────────────────┘
```

See Figure 1 for Description of Sample Extraction

Extract Hexane Extract with Sulfuric Acid*

Discard the Aqueous Layer

Wash the Hexane Layer with NaCl Solution

Discard the Aqueous Layer

Extract the Hexane with KOH Solution

Discard the Aqueous Layer

Wash the Hexane Layer with NaCl Solution

Discard the Aqueous Layer

Dry Extract with Na_2SO_4

Silica Gel Cleanup

Carbon Column Cleanup

Concentrate to Final Volume

Add Recovery Standard Solution

HRGC/HRMS Analyses

* Repeat this step until the aqueous layer is clear

Figure 2. Cleanup Procedure for Scrubber Water Sample

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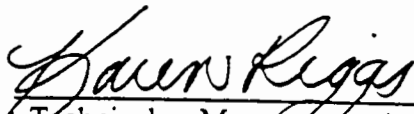
N-2
Battelle SOPs for D/F Analysis
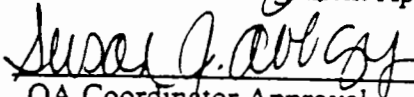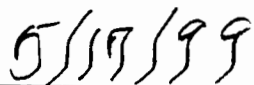
Title: Standard Operating Procedure for Polychlorinated Dibenzo-p-Dioxin/Polychlorinated Dibenzofuran (PCDD/PCDF) Sample Preparation Using Modified Method 8290
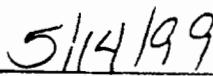
Number: SOP0802-02-01

The attached Standard Operating Procedure is recommended for approval and commits the laboratory to follow the elements described within.

_____
Technical or Management Approval

_____
QA Coordinator Approval

5/19/99
Date

5/14/99
Date

Distribution

This SOP is a controlled document which is maintained by the QA Coordinator and included in appropriate Quality Assurance Project Plans, as required.

A. Procedure

A1. Scope and Applicability
This SOP describes routine procedures for preparing samples for PCDD/PCDF analysis. These procedures follow general guidelines described in EPA Method 8290, with some minor modifications/improvements.

A2. Summary of Method
The purpose of this SOP is to provide a description of PCDD/PCDF sample preparation activities using modified Method 8290 procedures and covers the following:

- Sample collection, preservation, and handling
- Sample extraction and internal standard spiking
- Extract cleanup and
- Final concentration activities.

A3. Definitions
All references in this section are to SW846 Method 8290 unless otherwise indicated.

A4. Personnel Qualifications
Personnel assigned to laboratory activities meet the educational, work experience, and training requirements for their positions. Records on personnel qualifications and training are maintained in personnel files accessible for review during audit activities. Training is conducted in accordance with standard operating procedures and is available to all laboratory personnel. Employees must demonstrate proficiency at specific tasks and this capability is documented and kept in a central file.

A5. Sample Collection
All samples are collected according to Section 6.2 or as required by the client.

A6. Handling and Preservation

All samples are handled according to Section 6.2 or as required by the client.

A7. Sample Preparation and Analysis

Samples are spiked with internal standard and extracted using the matrix-specific techniques described in Section 7.0. Modifications to Section 7.0 include:

1. Fish Tissue (Section 7.2) – When a lipid determination is not required, a 10 g portion of the fish sample and 250 mL of hexane:methylene chloride (1:1) are used for extraction. Whether or not a lipid determination is required, the fish sample is mixed with 5 to 10 g Varian Hydromatrix drying agent until free flowing. The remaining fish tissue extraction follows that described in the method.

2. Soil/Sediment (Section 7.4.6) – The soil/sediment sample is mixed with 5 to 10 g of Varian Hydromatrix drying agent until free flowing. Toluene is used as the extraction solvent without a Dean Stark apparatus. The sample extract is typically not filtered through a glass fiber filter unless a significant amount of solids are present in the extract.

Hydromatrix is used as a drying agent rather than sodium sulfate since the time required for the sample-drying agent mixture to become free flowing is reduced when Hydromatrix is used. Samples prepared using Hydromatrix have yielded equivalent internal standard recoveries as those prepared using sodium sulfate.

Prior to all extractions, the sample/Hydromatrix mixture is spiked with an internal standards solution containing fifteen $^{13}C_{12}$-labeled PCDD/PCDF, as called for in Method 1613, Table 3 rather than nine as stated in Method 8290. The additional labeled PCDD/PCDF allow all but two of the isomers to be directly related to an internal standard for identification and quantification purposes. Use of this complete range of internal standards provides better accuracy than afforded by standard Method 8290.

Partition

The extracts are partitioned against acid and base solutions as described in Section 7.5.1 with the following modifications:

1. After the samples are transferred to the separatory funnels, the extracts are spiked with a cleanup standard (2,3,7,8-TCDD-^{37}Cl$_4$) as called for in Method 1613, Section 7.11. This cleanup standard is used to monitor the recovery of the analytes through the cleanup process.

2. Instead of the 40-mL acid, base, and salt washes that are specified in Method 8290, Section 7.5.1, the samples are subject to one 30-mL acid wash, successive 20-mL acid washes as needed to remove color, one 20 mL salt wash, one15-mL base wash, and two 20 mL salt washes. Reducing the volume of acid, base and salt solutions has proven non-deleterious to internal standard recoveries.

Silica/Alumina Column Cleanup

The extracts are put through silica and alumina columns in a manner similar to that called for in Section 7.5.2 with the following modifications:

Although the silica column is prepared as described in the method, the alumina column is prepared using 6 g of Sigma basic alumina. Both silica and alumina columns are rinsed independently with 20 mL of hexane. The columns are then stacked with the silica on top of the alumina and the sample extract is applied to the silica column. The stacked columns are rinsed with 100 mL of hexane which is discarded. The columns are separated so that 40 mL of hexane:methylene chloride (1:1) may be passed through the alumina column. The hexane:methylene chloride eluant is collected and concentrated to 1 mL for processing through a carbon column.

Utilizing this stacked column approach has proven non-deleterious to internal standard recoveries but has decreased sample preparation time and solvent usage. Procedures for the use of basic alumina are taken from Method 1613, Section 13.4.

Carbon Column Cleanup

The sample extracts are processed through a carbon column as described in Section 7.5.3 with the following modifications:

The carbon mixture that is used to pack the column consists of a 20% (w/w) mixture of Carbopack-C/Celite 545. Method 1613, Section 13.5 suggests the use of an 18% Carbopack/Celite mixture. A 20% Carbopack/Celite mixture was chosen in order to remove

more interferences from the sample extracts and to improve internal standard recoveries. When the column is packed, only glass wool, 0.55 g of the carbon mixture, and more glass wool are used. The additional plugs of Celite are not used.

The elution scheme is essentially the same as specified in Method 1613, Section 13.5 with the exception that the carbon columns are back-eluted with 30-mL toluene rather than 20 mL as specified in Section 13.5.5.

The final concentration and reconstitution of the sample extracts is significantly different than that described in Section 7.5.3.6 to accommodate transfer of the extract to GC autosampler vials: 20 :L of nonane is pipetted into muffled, methylene chloride-rinsed concentrator tubes. The tubes are lightly tapped to remove any air bubbles present and the meniscus is marked. 200 :L of hexane is pipetted into the tubes and the meniscus is marked. Leaving the solvents in the tubes, the sample extracts are transferred from round bottom flasks to tubes using 3 x 1 mL hexane rinses. The extracts are blown down to approximately 200 :L. The round bottom flasks are rinsed with 1 mL of methylene chloride which is transferred to the tubes and again concentrated to approximately 200 :L. The round bottom flasks are rinsed with 0.5 mL of methylene chloride which is transferred to the tubes and again concentrated to 200 :L. The extracts are spiked with 10 :L of the nonane recovery spiking solution and vortexed for 30 seconds. The extracts are blown down to the 20 :L meniscus level and then transferred to a GC vial for analysis. The above procedure has been proven as an effective and efficient method of concentrating the sample extracts for analysis.
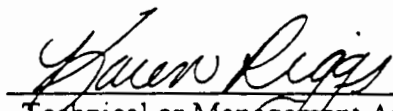
B. References
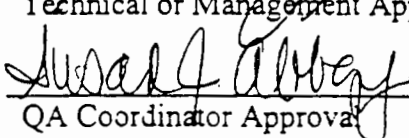
1. SW-846, Method 8290. Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRCG/HRMS), Revision 0, 1994.
2. EPA Method 1613: Tetra-Through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, Revision B, 1994, EPA 821-B-94-005.

Title: Standard Operating Procedure For The Analysis of Polychlorinated Dibenzo-p-Dioxin/Polychlorinated Dibenzofuran (PCDD/PCDF) Using High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) Using Modified Method 8290

Number: SOP0802-01-01

The attached Standard Operating Procedure is recommended for approval and commits the laboratory to follow the elements described within.

Technical or Management Approval   5/17/99
                                                            Date

QA Coordinator Approval   5/14/99
                                                            Date

Distribution

This SOP is a controlled document which is maintained by the QA Coordinator and included in appropriate Quality Assurance Project Plans, as required.

A. Procedure

A1. Scope and Applicability

This SOP describes routine procedures for HRGC/ HRMS analysis of samples for PCDD PCDF. These analyses follow general guidelines described in EPA Method 8290, with some minor modifications/improvements.

A2. Summary of Method

The purpose of this SOP is to provide a description of PCDD/PCDF sample analysis activities using modified Method 8290 procedures and covers the following:

- Chromatographic/Mass Spectrometric conditions and data acquisition parameters
- Calibration
- Analysis
- Calculations and
- System performance criteria.

A3. Definitions

VG, Fisons, and Micromass all refer to the same company, and may be used interchangeably

A4. Personnel Qualifications

Personnel assigned to laboratory activities meet the educational, work experience, and training requirements for their positions. Records on personnel qualifications and training are maintained in personnel files accessible for review during audit activities. Training is conducted in accordance with standard operating procedures and is available to all laboratory personnel. Employees must demonstrate proficiency at specific tasks and this capability is documented and kept in a central file.

A5. Apparatus and Materials

All calibration, column performance, window defining, recovery standards, internal standards spiking solutions, PARs, SRMs, etc. are obtained from commercial sources such as Cambridge Isotope Labs.

A6. Instrument or Method Calibration

The GC/HRMS instrumentation is calibrated at levels specified in Method 1613, Table 4 with one additional calibration standard at concentrations equivalent to ½ the level of Method 1613's lowest calibration point. The Method 1613 calibration solutions represent an expanded calibration concentration range compared to the calibration range in Method 8290.

Using the option in Method 1613, Section 10.2, only 1 ul of calibration solution or sample extract is injected per run, rather than 2 ul as specified in Method 8290, Section 7.7. The samples are injected on-column, rather than split-splitless as stated in Method 8290, Section 7.6.

For DB-5 continuing calibration analyses, a combination solution made by Cambridge Isotope Labs, composed of Calibration solution 3, window defining mixture, and tetra dioxin GC column performance mixture, is injected at the beginning and end of each 12 hour run period. The response factors are checked against the mean RRF from the initial calibration, and must fall within the +/- 20% RRF window for natives, and the +/- 30% window for ^{13}C-lableled compounds, unless otherwise specified by the client. This allows determination of calibration and column performance in a single run.

A7. Sample Preparation and Analysis

A.7.1 Sample Preparation

For sample preparation procedures, see *SOP for Polychlorinated Dibenzo-p-dioxin/Polychlorinated Dibenzofuran (PCDD/PCDF) Sample Preparation Using Modified Method 8290.*

A.7.2 Sample Analysis

The GC/MS parameters listed in Method 8290, section 7.6 are followed with the following exceptions. The GC column listed in Method 8290 is used, but the temperature program has a different initial temperature (140 C) to allow the solvent peak to elute slowly enough to not trip the source ion gauge. The upper temperature of the ramp is held to 320 C rather than 330 C to accommodate the upper temperature limit of the column.

All five groups (Tetra through Octa) are monitored separately. The mass for the cleanup standard $^{37}Cl_4$-2,3,7,8-TCDD, is also monitored per Method 1613, Table 8. Analysis is carried out as stated in Method 8290, Section 7.8.

A8. Data Acquisition, Calculations, and Data Reduction

Calculations are carried out using Opusquan, a software program designed for dioxin/furan analysis by VG/Micromass Co. Ltd. These calculations are the same as specified in Method 8290, Section 7.9. Estimated detection limit is calculated by measuring the sum of the heights of a native peak at the predicted retention time, times 2.5, divided by the total area of its internal standard ions, using the equation:

$$MDL = (F * Ni * Si * A/H * Qs) / (RRF * As * S)$$

Where

F = the user factor (dl_factor) in the form "fullrun"

Ni = the sum of the noise level of the analyte ions

Si = the sum of the "min_sig_to_noise" keyword value for each of the analyte ions

A/H = the mean area: height ratio of all ions of this analyte's internal standard

Qs = the internal standard amount

RRF = the mean relative response factor of the analyte

As = the total area of all internal standard ion peaks

S = the weight of the sample

A method blank is analyzed and processed using Opusquan in the "blank" mode. The noise factor for the natives in this blank run is then subtracted from subsequent runs, which are

processed in the "quantitation" mode to obtain an accurate detection limit for each analyte in each run.

A9. Computer Hardware and Software

Calculations are carried out using Opusquan, a software program designed for dioxin/furan analysis by VG/Micromass Co. Ltd.

B. Quality Control and Quality Assurance

B.1. System Performance Criteria

A combination calibration solution 3/window defining mixture/column performance mixture is injected at the beginning and end of each twelve-hour period. This is to ensure adequate resolution of the isomeric peaks, to ascertain that the windows are set correctly to see all the isomers in each congener group, and to verify that the HRMS is adequately tuned. A PFK resolution check is also hard-copied at the beginning and end of each GC/HRMS analysis batch to verify mass resolution.

C. References

1. SW-846, Method 8290. Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS), Revision 0, 1994.

2. EPA Method 1613: Tetra-Through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, Revision B, 1994, EPA 821-B-94-005.

3. VG Opusquan 2.0 Reference Manual, Issue 4, March 1995

4. Private communication from John Bill, Fisons Instruments, 04-20-95

N-3
PAH Protocols

California Environmental Protection Agency

⊜≣ Air Resources Board

Method 429

Determination of Polycyclic Aromatic
Hydrocarbon (PAH) Emissions
from Stationary Sources

Adopted: September 12, 1989
Amended: July 28, 1997

TABLE OF CONTENTS

FIGURES

APPENDIX A

Method 429

Determination of Polycyclic Aromatic Hydrocarbon (PAH) Emissions From Stationary Sources

1 INTRODUCTION

1.1 APPLICABILITY

This method applies to the determination of nineteen polycyclic aromatic hydrocarbons (PAH) in emissions from stationary sources. These are listed in Table 1. The sensitivity which can ultimately be achieved for a given sample will depend upon the types and concentrations of other chemical compounds in the sample as well as the original sample size and instrument sensitivity.

Any modification of this method beyond those expressly permitted shall be considered a major modification subject to approval by the Executive Officer of the California Air Resources Board or his or her authorized representative.

1.2 PRINCIPLE

Particulate and gaseous phase PAH are extracted isokinetically from the stack and collected on XAD-2 resin, in impingers, or in upstream sampling train components (filter, probe, nozzle). Only the total amounts of each PAH in the stack emissions can be determined with this method. It has not been demonstrated that the partitioning in the different parts of the sampling train is representative of the partitioning in the stack gas sample for particulate and gaseous PAH.

The required analytical method is isotope dilution mass spectrometry combined with high resolution gas chromatography. This entails the addition of internal standards to all samples in known quantities, matrix-specific extraction of the sample with appropriate organic solvents, preliminary fractionation and cleanup of extracts and analysis of the processed extract for PAH using high-resolution capillary column gas chromatography coupled with either low resolution mass spectrometry (HRGC/LRMS), or high resolution mass spectrometry (HRGC/HRMS). To ensure comparable results, the same MS method must be used for samples collected at all tested locations at those sources where more than one location is tested.

Minimum performance criteria are specified herein which must be satisfied to ensure the quality of the sampling and analytical data.

1.3 DEFINITIONS AND ABBREVIATIONS

1.3.1 Internal Standard

An internal standard is a ^{2}H-labelled PAH which is added to all field samples, blanks and other quality control samples before extraction. It is also present in the calibration solutions. Internal standards are used to measure the concentration of the analyte and surrogate compounds. There is one internal standard assigned to each of the target analytes and surrogates.

1.3.2 Surrogate Standard

A surrogate standard is a labelled compound added in a known amount to the XAD-2 resin of the sampling train, and allowed to equilibrate with the matrix before the gaseous emissions are sampled. The surrogate standard has to be a component that can be completely resolved, is not present in the sample, and does not have any interference effects. Its measured concentration in the extract is an indication of the how effectively the sampling train retains PAH collected on the XAD-2 resin. The recovery of the surrogate standards in the field blanks can be used to determine whether there are any matrix effects caused by time or conditions under which the sample is transported and stored prior to analysis.

1.3.3 Alternate Standard

An alternate standard is a ^{2}H-labelled PAH compound which is added to the impinger contents prior to extraction to estimate the extraction efficiency for PAHs in the impinger sample

1.3.4 Recovery Standard

A recovery standard is a ^{2}H-labelled PAH compound which is added to the extracts of all field samples, blanks, and quality control samples before HRGC/MS analysis. It is also present in the calibration solution. The response of the internal standards relative to the recovery standard is used to estimate the recovery of the internal standards. The internal standard recovery is an indicator of the overall performance of the analysis.

1.3 5 Relative Response Factor

The relative response factor is the response of the mass spectrometer to a known amount of an analyte or labelled compound (internal standard or surrogate standard) relative to a known amount of an internal standard or another labelled compound (recovery standard or internal standard).

1.3.6 Performance Standard

A performance standard is a mixture of known amounts of selected standard compounds. It is used to demonstrate continued acceptable performance of the GC/MS system. These checks include system performance checks, calibration checks, quality checks, matrix recovery, and surrogate recoveries.

1.3.7 Performance Evaluation Sample

A performance evaluation sample is one prepared by EPA or other laboratories that contains known concentrations of method analytes, and has been analyzed by multiple laboratories to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Concentrations must be in the same range as typical field samples. Analyte concentrations are not known by the analyst.

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1.3.8 Laboratory Control Sample

A laboratory control sample is one that contains known concentrations of method analytes that is analyzed by a laboratory to demonstrate that it can obtain acceptable identifications and measurements with procedures to be used to analyze field samples containing the same analytes. Analyte concentrations are known by the analyst. The laboratory must prepare the control sample from stock standards prepared independently from those used for calibration.

1.3.9 End User

The regulating agency shall be considered the end user if this test method is conducted for regulatory purposes, or the regulating agency shall designate the end user for the purposes of this method. Otherwise the end user shall be the party who defrays the cost of performing this test method. In any case, the pre-test protocol (Section 2) must identify the end user.

1.3.10 Tester

Usually the tester is a contract engineering firm that performs the sampling procedures and delegates responsibility for specific analytical procedures to an analytical group (usually part of a subcontracting laboratory firm). In some cases, the tester may be part of the regulating agency. The tester shall be the party ultimately responsible for the performance of this test method whether directly or indirectly through the co-ordination of the efforts of the analytical group and the efforts of the sampling group.

1.3.11 Analyst

This term refers to the analytical group that performs the analytical procedures to generate the required analytical data.

1.3.12 Source Target Concentration

This is the target concentration for each emitted PAH of interest specified by the end user of the test results. The target concentration shall be expressed in units of mass of target substance per volume of emissions; typical units are nanograms per dry standard cubic meter or micrograms per dry standard cubic meter (ng/dscm or µg/dscm)

1.3.13 The Method Detection Limit

The method detection limit (MDL) is based on the precision of detection of the analyte concentration near the detection limit. It is the product of the standard deviation of seven replicate analyses of resin samples spiked with low concentrations of the analyte and Student's t value for 6 degrees of freedom at a confidence level of 99%.

1.3.14 The Practical Quantitation Limit

The practical quantitation limit (PQL) is a limit for each compound at or below which data must not be reported. It is the minimum sample mass that must be collected in the sampling train to allow detection during routine laboratory operation within the precision limits established by the

MDL determination. The PQLs will be estimated at 5 times the MDL for those PAH that are not contaminants of the resin. The PQL for the remainder will be estimated at 5 times the blank XAD-2 resin level.

2 THE SOURCE TEST PROTOCOL

Every performance of this test method shall have an identified operator of the source to be tested, an identified end user of the test method results, and an identified tester who performs this test method. Figure 1 is a summary of the responsibilities of the parties involved in the coordination and performance of the source test. The protocol for the entire test procedure should be understood and agreed upon by the responsible parties prior to the start of the test.

2.1   RESPONSIBILITIES OF THE END USER AND THE TESTER

2.1.1   The End User

Before testing may begin, the end user of the test results (1.3.9) shall specify a source target concentration for each of the PAH to be determined by this method using the guidelines of Section 2.2.1.

The end user shall approve the source test protocol only after reviewing the document and determining that the minimum pre-test requirements (Sections 2.2 to 2.5) have been met.

2.1.2   The Tester

The tester (1.3.10) shall have the primary responsibility for the performance of the test method, and shall co-ordinate the efforts of the analytical group and the efforts of the sampling group

The tester shall be responsible for the selection of an analyst with documented experience in the satisfactory performance of the method. The tester shall obtain from the analyst all of the analytical data (Section 2.3) that are required for pre-test calculations of sampling parameters

Before performing the rest of this method, the tester shall develop and write a source test protocol (Section 2.2) to help ensure that useful test method results are obtained. The tester shall plan the test based on the information provided by the end user, the results of pre-test surveys of the source, and the tester's calculations of target source testing parameters (Section 2.2).

The tester shall be responsible for ensuring that all of the sampling and analytical reporting requirements (Section 10) are met.

2.1.3   The Analyst

The analyst shall be responsible for performing all of the required analytical procedures described in this test method and reporting the results as required by Sections 2.3, 4.2.1, 4.2.2, 10.1.1, 10.1.2, 10.1.3, and 10.2).

2.2 PRE-TEST REQUIREMENTS

The source test protocol shall specify the test performance criteria of the end user and all assumptions, required data and calculated targets for the following testing parameters:

(1) source target concentration of each emitted PAH of interest (2.2.1),

(2) preliminary analytical data (2.3) for each target PAH, and

(3) planned sampling parameters (2.5.4, 2.5.5, and 2.5.6).

The protocol must demonstrate that the testing parameters calculated by the tester will meet the needs of the end user. The source test protocol shall describe the procedures for all aspects of the source test including information on supplies, logistics, personnel and other resources necessary for an efficient and coordinated test.

The source test protocol shall identify the end user of the results, the tester, the analytical group, and the sampling group, and the protocol shall be signed by the end user of the results and the tester.

The tester shall not proceed with the performance of the remainder of this method unless the source test protocol is signed by the tester and the end user.

2.2.1 Source Target Concentration (STC)

The tester shall not proceed with the test unless a target concentration has been chosen. This will be the primary reporting objective of the emissions test. The end user shall select a basis for determining each target concentration from: a) regulatory limits, b) environmental risk assessments, and (c) the interests of the end user, the tester, and the stationary source.

2.2.1.1 Regulatory Limits

The regulatory limit shall be the basis for determining a target concentration for stationary source emissions in those cases where the purpose of the emissions test is to demonstrate compliance with the established regulatory limit.

2.2.1.2 Environmental Risk Assessments

In some cases testing is conducted for an environmental risk assessment. A pre-test estimate of the permissible risk shall then be used to determine the target concentration for stationary source emissions.

Note that some risk assessment methodologies will assume that a PAH is present at the detection limit or one half of the detection limit even when the compound is not detected. This is inappropriate for planning for the performance of the test method because by definition a substance cannot be detected at one half of its detection limit. In such cases, the target sampling parameter must be the maximum practical sample volume.

2.2.1.3   Interests of the End User, the Tester and the Stationary Source

In cases where the emissions test is not being performed to demonstrate compliance with a regulation, nor is it required for a risk assessment, the end user may use emissions results from previous tests of the facility or from similar facilities.

If estimates of the emissions are not available, the tester must conduct a preliminary-test at each emissions point of interest. This target concentration is necessary for the calculation of the target sampling parameters required by Section 2.5. Therefore, the emissions measured during the preliminary test must be representative of source operation. The tester must document operating conditions, and know from historical data, the extent to which the results of this preliminary run are representative of emissions from the source. This will require documentation of operating conditions during the preliminary test, and a knowledge of the potential variability in emissions with differences in source operation.

As an alternative to conducting a preliminary test, the end user may specify, as a sampling target, the longest practical sampling time so as to obtain the lowest practically achievable source reporting limit (Section 2.5.6).

2.3   REQUIRED PRELIMINARY ANALYTICAL DATA

2.3.1   Results of Blank Contamination Checks

The tester must obtain from the analyst the results of the PAH contamination checks. The analytical report must satisfy the reporting requirements of Sections 10 and 10.1.

The analyst shall use the procedures described in Sections 4.2.1 and 4.2.2 to clean the sampling media (filters and XAD-2 resin) and check for PAH contamination.

Table 3 shows the results of analyses of different lots of re-cleaned XAD-2 resin. The purpose of this table is to show typical variability. Actual results may vary from one test to another.

2.3.2   The Method Detection Limit

The method detection limit (MDL) must be determined by the same analyst (1.3.11) that will perform the analyses subsequent to sampling. Before estimating the method detection limit (MDL), the analyst shall identify those PAH that are contaminants of the XAD-2 resin using the procedures described in Sections 4.2.2.1 to 4.2.2.4. The analyst shall determine the MDL as described in Section 8.3 and Appendix A.

2.3.3   The Practical Quantitation Limit

The analyst shall calculate the practical quantitation limits (PQLs) for the target PAH. This value will be 5 times the MDL or 5 times the XAD-2 background level for those compounds that have been identified by the analyst as contaminants.

Table 2 lists practical quantitation limits obtained during ARB's development of this method. The values for the PQLs will vary with the performance of individual laboratories. Therefore, the tester must obtain PQL values for all of the target analytes from the analyst.

2.4 EXPECTED RANGE IN TARGET CONCENTRATIONS OF INDIVIDUAL PAHs

The PAH compounds in a source test sample can show large differences in concentrations. A sample that might provide sufficient analyte for the detection and quantitation of the lowest concentration PAH could contain levels of other PAHs that exceed the upper limit of the method.

In some cases the solution is two GC/MS injections - first with the undiluted extract, and then again after appropriate dilution of the extract. At other times the required minimum dilution might be so large as to result in the reduction of the internal standard response below the minimum required by the method. With prior notification of expected levels of the target analytes, the analyst can modify the preparation of the samples so that useful results might be obtained. All major modifications must be approved by the Executive Officer.

2.5 SAMPLING RUNS, TIME, AND VOLUME

2.5.1 Sampling Runs

A test shall include at least three sampling runs in series and a blank sampling train.

2.5.2 Minimum Sample Volume (MSV)

This is the minimum sample volume that must be collected in the sampling train to provide the minimum reportable mass of PAH for quantitation. It must be based on a) the practical quantitation limit (2.3.3), b) the source target concentration (2.2.1), and c) sampling limitations. Use Equation 429-1 to calculate the target MSV for each PAH analyte.

$$MSV(dscm) = PQL \times \frac{1}{STC} \qquad 429\text{-}1$$

--- Where:

PQL = The practical quantitation limit, ng/sample (Section 2.3.3)
STC = The source target concentration, ng/dscm (Section 2.2.1)

2.5.3 Minimum Sampling Time (MST)

This is the minimum time required to collect the minimum sample volume at the expected average volumetric sampling rate (VSR). Use Equation 429-2 to calculate the minimum sampling time (MST) required to collect the minimum sample volume calculated in Section 2.5.2. The tester must use an average volumetric sampling rate (VSR) appropriate for the source to be tested.

$$MST \text{(hours)} = \frac{MSV}{VSR} \times \frac{1}{0.028317} \times \frac{1}{60} \qquad\qquad 429\text{-}2$$

Where:

VSR	=	Expected average volumetric sampling rate, dscfm
60	=	Factor to convert minutes to hours
0.028317	=	Factor to convert dscf to dscm

The end user must decide whether the MSTs are all practically feasible and whether they can be increased to allow for any deviation from the sampling and analytical conditions assumed by the test plan. Based on this decision, the tester must use either Section 2.5.4 (a) or 2.5.4 (b) to calculate a planned sample volume (PSV).

2.5.4 Planned Sample Volume (PSV)

This is the volume of emissions that must be sampled to provide the target analytes at levels between the PQL and the limit of linearity. The planned sample volume is the primary sampling target whenever practically feasible. The PSV is calculated according to either 2.5.4 (a) or 2.5.4 (b).

(a) If the end user has decided that the MSTs can be increased, the tester must use Equation 429-3 to calculate the PSV using the largest of the 19 MSV values calculated in Section 2.5.2. and the largest value for F that will give a practically achievable sample volume that provides the target analytes at levels between the PQL and the limit of linearity. Use this PSV to calculate the planned sampling time (Section 2.5.5 a) and Equation 429-6.

(b) If the MSTs are not all practically achievable, the tester and the end user must agree on a maximum practical sampling time (Section 2.5.5b). This value must then be used for the PST in Equation 429-4 to calculate the PSV. The tester must identify in the source test protocol the target analytes for which the PSV is lower than the MSV. The primary reporting objective of the test cannot be achieved for those analytes. If the primary reporting objective cannot be achieved for all of the target analytes, it must be discussed in the protocol and the alternative reporting objective (Section 2.5.6) must be approved by the end user of the results.

The volume of sample that is actually collected will be determined by practical sampling limitations intended use of the data and the level of uncertainty that the end user can

tolerate in the measurement of the target concentrations. This uncertainty will decrease as the value of F (Equation 429-5) increases.

$$PSV(dscm) = MSV \times F \qquad 429\text{-}3$$

$$PSV(dscm) = PST \times VSR \qquad 429\text{-}4$$

$$F = \frac{PSV}{MSV} \qquad 429\text{-}5$$

Where:

PST = Planned sampling time from Section 2.5.5
F = A safety factor (>1) that allows for deviation from ideal sampling and analytical conditions

2.5.5 Planned Sampling Time (PST)

Two options are available for calculating the planned sampling time depending on whether the primary objective can be achieved for all of the target analytes.

(a) The planned sampling time (PST) shall be long enough to 1) collect the planned sample volume with reportable levels of the target analytes and 2) sample representative operating conditions of the source. If the average sampling rate (VSR) used to estimate the planned sampling time cannot be achieved in the field (Section 4.4.4.1), the sampling time must be recalculated using the actual VSR and the target PSV in equation 429-6.

(b) The planned sampling time shall be a practical maximum approved by the end user and it shall be long enough to sample representative operating conditions of the source.

$$PST(hours) = \frac{PSV}{VSR} \times \frac{1}{0.028317} \times \frac{1}{60} \qquad 429\text{-}6$$

2.5.6   Preliminary Estimate of Source Reporting Limit (SRL)

Before the test proceeds, the end user and the tester shall agree on a preliminary estimate of the source reporting limit for each target PAH. The SRL shall be calculated using Equation 429-7. The planned sample volume will contain reportable levels of a given analyte if that analyte is present in the emissions at a concentration that is equal to or greater than the calculated SRL.

$$SRL\,(ng/dscm) = \frac{PQL}{PSV} \qquad\qquad 429\text{-}7$$

Where:

SRL = Preliminary estimate of source reporting limit, ng/dscm
PQL = Practical quantitation limit, ng
PSV = Planned sample volume, dscm

2.5.7   Example Calculations

Figure 9 B is an example of the minimum required calculations of sampling parameters for the source test protocol.

3   INTERFERENCES

Interferences may be caused by contaminants in solvents, reagents, sorbents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated backgrounds at the ions monitored. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 6.1.1.

The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

Transformation of PAH and the formation of artifacts can occur in the sampling train. PAH degradation and transformation on sampling train filters have been demonstrated. Certain reactive PAH such as benzo[a]pyrene, benzo[a]anthracene, and fluoranthene when trapped on filters can readily react with stack gases. These PAH are transformed by reaction with low levels of nitric acid and higher levels of nitrogen oxides, ozone, and sulfur oxides.-

PAH degradation may be of even greater concern when they are trapped in the impingers. When stack gases such as sulfur oxides and nitrogen oxides come in contact with the impinger water they are converted into sulfuric acid and nitric acid respectively. There is evidence that under such conditions certain PAH will be degraded. It is recommended that the PAH levels in the impingers be used as a qualitative tool to determine if breakthrough has occurred in the resin.

4   SAMPLING APPARATUS, MATERIALS AND REAGENTS

4.1   SAMPLING APPARATUS

The sampling train components listed below are required. All surfaces which may come in contact with the sample or recovery solvents shall be of quartz, borosilcate glass or Teflon. The tester may use an alternative to the required sampling apparatus only if, after review by the Executive Officer, it is deemed equivalent for the purposes of this test method.

Mention of trade names or specific products does not constitute endorsement by the California Air Resources Board. In all cases, equivalent items from other suppliers may be used.

A schematic of the sampling train is shown in Figure 2. The train consists of nozzle, probe, heated particulate filter, condenser, and sorbent module followed by three impingers and a silica gel drying cartridge. An in-stack filter may not be used because at the in-stack temperatures the filter material must be of a material other than the Teflon required by the method. A cyclone or similar device in the heated filter box may be used for sources emitting a large amount of particulate matter.

For sources with a high moisture content, a water trap may be placed between the heated filter and the sorbent module. Additional impingers may also be placed after the sorbent module. If any of these options are used, details must be provided in the test report. The train may be constructed by adaptation of an ARB Method 5 train. Descriptions of the train components are contained in the following sections.

4.1.1   Probe Nozzle

Quartz, or borosilicate glass with sharp, tapered leading edge. The angle of taper shall be 30° and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise approved by the Executive Officer.

A range of sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (1/8 to 1/2 in.) - or larger if higher volume sampling trains are used - inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in Section 5.1 of ARB method 5.

4.1.2   Probe

The probe must be lined or made of Teflon, quartz, or borosilicate glass. Other inert materials may be used only if they have been approved by the Executive Officer. The liner or probe extends past the retaining nut into the stack. A temperature-controlled jacket provides protection of the liner or probe. The liner shall be equipped with a connecting fitting that is capable of forming a leak-free, vacuum tight connection without the use of sealing greases.

4.1.3   Preseparator

A cyclone, a high capacity impactor or other device may be used if necessary to remove the majority of the particles before the gas stream is filtered. This catch must be used for any

subsequent analysis. The device shall be constructed of quartz or borosilicate glass. Other inert materials may be used subject to approval by the Executive Officer.

4.1.4   Filter Holder

The filter holder shall be constructed of borosilicate glass, with a Teflon frit or Teflon coated wire support and glass-to-glass seal or Teflon gasket. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe, cyclone, or nozzle depending on the configuration used. Whenever "O" ring seals are used, they shall be of Teflon or Teflon coated material. Other inert holder and gasket materials may be used subject to approval by the Executive Officer.

4.1.5   Sample Transfer Line

The sample transfer line shall be Teflon (1/4 in. O.D. x 1/32 in. wall) with connecting fittings that are capable of forming leak-free, vacuum tight connections without using sealing greases. The line should be as short as possible.

4.1.6   Condenser

The condenser shall be constructed of borosilicate glass and shall be designed to allow the cooling of the gas stream to at least 20°C before it enters the sorbent module. Design for the normal range of stack gas conditions is shown in Figure 3.

4.1.7   Sorbent Module

The sorbent module shall be made of glass with connecting fittings that are able to form leak-free, vacuum tight seals without the use of sealant greases (Figure 3). The vertical resin trap is preceded by a coil-type condenser, also oriented vertically, with circulating cold water. Gas entering the sorbent module must have been cooled to 20°C (68°F) or less. The gas temperature shall be monitored by a thermocouple placed either at the inlet or exit of the sorbent trap. The sorbent bed must be firmly packed and secured in place to prevent settling or channeling during sample collection. Ground glass caps (or equivalent) must be provided to seal the sorbent-filled trap both prior to and following sampling. All sorbent modules must be maintained in the vertical position during sampling.

4.1.8   Impinger Train

Connect three or more impingers in series with ground glass fittings able to form leak-free, vacuum tight seals without sealant greases. Whenever "O" ring seals are used, they shall be of Teflon or Teflon coated material. All impingers shall be of the Greenburg-Smith design modified by replacing the tip with a 1.3 cm (1/2 in.) I.D. glass tube extending to 1.3 cm (1/2 in.)from the bottom of the flask.

The first impinger may be oversized for sampling high moisture streams. The first and second impingers shall contain 100 mL of 3 mM sodium bicarbonate ($NaHCO_3$) and 2.4 mM sodium carbonate (Na_2CO_3) (Section 4.2.5). This is intended to neutralize any acids that might form in

the impingers. The third impinger shall be empty. Silica gel shall be added to the fourth impinger.

A thermometer which measures temperatures to within 1°C (2°F), shall be placed at the outlet of the third impinger.

4.1.9   Silica Gel Cartridge

This may be used instead of a fourth impinger. It shall be sized to hold 200 to 300 gm of silica gel.

4.1.10   Pitot Tube

Type S, as described in Section 2.1 of ARB Method 2 or other devices approved by the Executive Officer. The pitot tube shall be attached to the probe extension to allow constant monitoring of the stack gas velocity as required by Section 2.1.3 of ARB Method 5. When the pitot tube occurs with other sampling components as part of an assembly, the arrangements must meet the specifications required by Section 4.1.1 of ARB Method 2. Interference-free arrangements are illustrated in Figures 2-6 through 2-8 of ARB Method 2 for Type S pitot tubes having external tubing diameters between 0.48 and 0.95 cm (3/16 and 3/8 in.).

Source-sampling assemblies that do not meet these minimum spacing requirements (or the equivalent of these requirements) may be used only if the pitot tube coefficients of such assemblies have been determined by calibration procedures approved by the Executive Officer.

4.1.11   Differential Pressure Gauge

Two inclined manometers or equivalent devices, as described in Section 2.2 of ARB Method 2. One manometer shall be used for velocity head (ΔP) readings and the other for orifice differential pressure readings.

4.1.12   Metering System

Vacuum gauge, leak-free pump, thermometers accurate to within 3°C (5.4°F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 2. Other metering systems must meet the requirements stated in Section 2.1.8 of ARB Method 5.

4.1.13   Barometer

Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

4.1.14 Gas Density Determination Equipment

Temperature sensor and pressure gauge, as described in Section 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The preferred configuration and alternative arrangements of the temperature sensor shall be the same as those described in Section 2.1.10 of ARB Method 5.

4.1.15 Filter Heating System

The heating system must be capable of maintaining a temperature around the filter holder during sampling of $(120\pm14°C)$ $(248\pm25°F)$. A temperature gauge capable of measuring temperature to within $3°C$ $(5.4°F)$ shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling.

4.1.16 Balance

To weigh the impingers and silica gel cartridge to within 0.5 g.

4.2 SAMPLING MATERIALS AND REAGENTS

4.2.1 Filters

The filters shall be Teflon coated glass fiber filters without organic binders, or Teflon membrane filters, and shall exhibit at least 99.95 percent efficiency (0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard Method D 2986-71 (Reapproved 1978). Test data from the supplier's quality control program are sufficient for this purpose. Record the manufacturer's lot number.

4.2.1.1 Contamination Check of Filter

The tester must have the filters cleaned by the analyst and checked for contamination prior to use in the field. The contamination check must confirm that there are no PAH contaminants present that will interfere with the analysis of the sample PAHs of interest at the target reporting limits. The analyst must record the date the filter was cleaned.

The filters shall be cleaned in batches not to exceed 50 filters. To clean the filters, shake for one hour in methylene chloride in a glass dish that has been cleaned according to Section 6.2 After extraction, remove the filters and dry them under a clean N_2 stream. Analyze one filter using the same extraction, clean-up and analysis procedures to be used for the field samples (Sections 6.5.1.2, 6.6, and 7.5).

$$\frac{\text{Blank value}}{\text{per filter}} = \frac{\text{Total mass (ng) of analyte}}{\text{No. filters extracted}} \qquad 429\text{-}8$$

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The acceptance criteria for filter cleanliness depends on 1) the method reporting limit. 2) the expected field sample volume and 3) the desired reporting limit for the sampled emissions stream. Filters with PAH levels equal to or greater than the target reporting limit for the analyte(s) of concern shall be rejected for field use.

If the filter does not pass the contamination check, re-extract the batch and analyze a clean filter from the re-extracted batch. Repeat the re-extraction and analysis until an acceptably low background level is achieved. Store the remainder tightly wrapped in clean hexane-rinsed aluminum foil as described in Section 4.3.3.

Record the date of the last cleaning of the filters and the date of the PAH analysis, and prepare a laboratory report of the analytical results that includes all of the information required by Section 10.2.

The tester shall obtain this laboratory report with the date of cleaning of the filters, and the date of the filter contamination check from the analyst, and report them in the source test protocol and the test report as required by Sections 10.1 and 10.3.

4.2.2 Amberlite XAD-2 Resin

The XAD-2 resin must be purchased precleaned and then cleaned again as described below before use in the sampling train.

4.2.2.1 Cleaning XAD-2 Resin

This procedure must be carried out in a Soxhlet extractor which will hold enough XAD-2 for several sorbent traps, method blanks and QC samples. Use an all glass thimble containing an extra coarse frit for extraction of the XAD-2. The frit is recessed 10 to 15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and stainless steel screen to prevent floating on the methylene chloride.

Clean the resin by two sequential 24 hour Soxhlet extractions with methylene chloride. Replace with fresh methylene chloride after the first 24 hour period.

4.2.2.2 Drying Cleaned XAD-2 Resin

The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. A 10.2 cm ID Pyrex pipe 0.6 m long with suitable retainers as shown in Figure 4 will serve as a satisfactory column. Connect the liquid nitrogen cylinder to the column by a length of cleaned 0.95 cm ID copper tubing, coiled to pass through a heat source. A convenient heat source is a water bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40°C.

Continue the flow of nitrogen through the adsorbent until all the residual solvent is removed. The rate of flow should be high enough that the particles are gently agitated but not so high as to cause the particles to break up.

4.2.2.3   Residual Methylene Chloride Check.

Extraction: Weigh a 1.0 g sample of dried resin into a small vial, add 3 mL of hexane, cap the vial and shake it well.

Analysis: Inject a 2 μL sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft x 1/8 in stainless steel containing 10% OV-101 on 100/120 Supelcoport.

Carrier Gas: Helium at a rate of 30 mL/min.

Detector: Flame ionization detector operated at a sensitivity of 4×10^{-11} A/mV.

Injection Port
Temperature: 250°C.

Detector
Temperature: 305°C.

Oven
Temperature: 30°C for 4 min; programmed to rise at 40°C per min until it reaches 250°C; return to 30°C after 1000 seconds.

Compare the results of the analysis to the results from a reference solution prepared by adding 2.5 μL of methylene chloride into 100 mL of hexane. This corresponds to 100 μg of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 μg/g of adsorbent. If the methylene chloride in the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

4.2.2.4   Contamination Check of XAD-2 Resin

The cleaned, dried XAD-2 resin must be checked for PAH contamination. Analyze a sample of the resin equivalent in size to the amount required to charge one sorbent cartridge for a sampling train. The extraction, concentration, cleanup and GC/MS analytical procedures shall be the same for this sample as for the field samples (Sections 6.5.1.2, 6.6, and 7.5).

The acceptance limit will depend on the PQL, the expected concentration in the sampled gas stream, and the planned sample volume. The contamination level must be less than the PQL or no more than 20 percent of the expected sample level.

If the cleaned resin yields a value for a target analyte which is not acceptable for the end user's intended application of the test results, repeat the extraction unless the analyst has historical data that demonstrate that re-extraction cannot reasonably be expected to further reduce the contamination levels. The tester must obtain these data from the analyst and include them in both the source test protocol and the emissions test report.

The contamination check shall be repeated if the analyst does not have such historical data. The analyst shall reclean and dry the resin (4.2.2.1, 4.2.2.2, and 4.2.2.3) and repeat the PAH analysis of the re-cleaned resin. If the repeat analysis yields a similar result to the first, record the contamination level for both the initial cleaning and the re-cleaning.

The analyst shall record the dates of the cleaning and extraction of the resin, and prepare a laboratory report of the analytical results that includes all of the information required by Section 10.2.

The tester shall obtain the dates of cleaning and the laboratory report of the results of the contamination check from the analyst, and report them in both the source test protocol and the emissions test report as required by Sections 10.1 and 10.3.

The tester shall identify the analytes for which the PQLs will be based on a blank contamination value, and calculate the PQLs as required by Section 2.3.3.

4.2.2.5   Storage of XAD-2 Resin

After cleaning, the resin may be stored in a wide mouth amber glass container with a Teflon-lined cap, or placed in one of the glass adsorbent modules wrapped in aluminum foil and capped or tightly sealed with Teflon film at each end. The containers and modules shall then be stored away from light at temperatures 4°C or lower until the resin is used in the sampling train.

The adsorbent must be used within twenty one (21) days of cleaning. If the adsorbent is not used within 21 days, it must be re-checked for contamination before use.

4.2.3   Silica Gel

Indicating type, 6 to 16 mesh. If previously used, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received. Alternatively, other desiccants (equivalent or better) may be used, subject to approval by the Executive Officer.

4.2.4   Reagent Water

Deionized, then glass-distilled, and stored in hexane- and methylene chloride-rinsed glass containers with TFE-lined screw caps.

4.2.5   Impinger Solution

Sodium bicarbonate 3 mM, and sodium carbonate 2.4 mM. Dissolve 1.0081 g sodium bicarbonate (NaHCO$_3$) and 1.0176 g of sodium carbonate (Na$_2$CO$_3$) in reagent water (4.2.4), and dilute to 4 liters.

4.2.6   Crushed Ice

Place crushed ice in the water bath around the impingers.

4.2.7 Glass Wool

Clean by methylene chloride soxhlet extraction for 16 hours. Air dry in a clean container in a clean hood. Store in methylene chloride washed glass jar with TFE-lined screw cap.

4.2.8 Chromic Acid Cleaning Solution

Dissolve 200 g of sodium dichromate in 15 mL of reagent water, and then carefully add 400 mL of concentrated sulfuric acid.

4.3 PRE-TEST PREPARATION

The positive identification and quantitation of PAH in an emissions test of stationary sources are strongly dependent on the integrity of the samples received and the precision and accuracy of all analytical procedures employed. The QA procedures described in Sections 4.3.7 and 8 are to be used to monitor the performance of the sampling methods, identify problems, and take corrective action.

4.3.1 Calibration

All sampling train components shall be maintained and calibrated according to the procedure described in APTD-0576 (Section 11.7), unless otherwise specified herein. The tester shall maintain a record of all calibration data.

4.3.1.1 Probe Nozzle

Probe nozzles shall be calibrated according to the procedure described in ARB Method 5.

4.3.1.2 Pitot Tube

Calibrate the Type S pitot tube assembly according to the procedure described in Section 4 of ARB Method 2.

4.3.1.3 Metering System

Calibrate the metering system before and after use according to the requirements of Section 5.3 of ARB Method 5.

4.3.1.4 Temperature Gauges

Use the procedure in Section 4.3 of ARB Method 2 to calibrate in-stack temperature gauges. Dial thermometers, such as those used for the dry gas meter and condenser outlet, shall be calibrated against mercury-in-glass thermometers.

4.3.1.5 Leak-Check of Metering System Shown in Figure 1

The tester shall use the procedure described in Section 5.6 of ARB Method 5

4.3.1.6   Barometer

                 Calibrate against a mercury barometer.

4.3.2   Cleaning Glassware for Sampling and Recovery

All glass parts of the train upstream of and including the sorbent module and the first impingers
shall be cleaned as described in Section 3A of the 1974 issue of Manual of Analytical Methods
for Analysis of Pesticide Residues in Human and Environmental Samples (Reference 11.4).
Take special care to remove residual silicone grease sealants on ground glass connections of used
glassware. These greasy residues shall be removed by soaking several hours in a chromic acid
cleaning solution (4.2.8) prior to routine cleaning as described above. Other cleaning procedures
may be used as long as acceptable blanks are obtained. Acceptance criteria for blanks are stated
in Section 8.2.

Rinse all glassware with acetone, hexane, and methylene chloride prior to use in the PAH
sampling train.

Glassware used in sample recovery procedures must be rinsed as soon as possible after use with
the last solvent used in it. This must be followed by detergent washing with hot water, and rinses
with tap water, deionized water, acetone, hexane, and methylene chloride. Other cleaning
procedures may be used as long as acceptable blanks are obtained. Acceptance criteria for
blanks are stated in Section 8.2.

4.3.3   Preparation of Filter

The clean dry filter (4.2.1) must be kept tightly wrapped in hexane-rinsed aluminum foil and
stored at 0 to 4°C in a container away from light until sampling. Before inserting the filter in the
sampling train, check visually against light for irregularities and flaws or pinhole leaks.

4.3.4   Preparation of Sorbent Cartridge, Method Blank, and
                 Laboratory Control Samples

Sorbent Cartridge

Use a sufficient amount (at least 30 gms or 5 gms/m^3 of stack gas to be sampled) of cleaned
resin to completely fill the glass sorbent cartridge which has been thoroughly cleaned as
prescribed (4.2.2).

Add the required surrogate standards (Table 7) to the sorbent cartridges for all of the sampling
and blank trains for each series of test runs. Follow the resin with hexane-rinsed glass wool, cap
both ends, and wrap the cartridge in aluminum foil. Store the prepared cartridges as required by
Section 4.3.5.

The sorbent cartridges must be loaded, and the surrogate standards must be added to the resin in
a clean area in the laboratory. There must be no turnaround of a used cartridge in the field.

The analyst shall record the date that the surrogate standards were added to the resin and the amount of each compound. The tester shall obtain these data from the analyst and report them in the source test protocol and the test report.

The appropriate levels for the surrogate standards are given in Table 7 which shows the spiking plan for surrogate standards, internal standards, alternate standards, and recovery standards. All of these required compounds are generally available. Additional labelled PAH may also be used if available. The labelled compounds used as surrogate standards must be different from the internal standards used for quantitation, and from the alternate and recovery standards. If the spiking scheme (Table 7) is modified, the tester must demonstrate that the proposed modification will generate data of satisfactory quality. Table 7A shows an approved modification that has been used in ARB's method development. All modifications must be approved by the Executive Officer before the emissions test is performed.

Laboratory Method Blank

Take a sample of XAD-2 resin from the same batch used to prepare the sampling cartridge. This will serve as the laboratory method blank (Section 8.1.1). The mass of this sample must be the same as that used in the sampling train. Spike with the same surrogate standards at the same levels used in the sampling cartridges.

Laboratory Control Sample

Set aside two samples of XAD-2 resin from the same batch used to prepare the sampling cartridge. These will serve as the laboratory control samples. (Section 8.1.3). The mass of each sample must be the same as that used in the sampling train.

4.3.5   Storage of Prepared Cartridges, Method Blank and Laboratory Control Sample

Store the aluminum foil wrapped sorbent cartridges away from light at 4°C or lower until they are fitted into the sampling trains. Do not remove the caps before the setup of the sampling train.

The maximum storage time from cleaning of the resin to sampling with the spiked resin cartridge must not exceed 21 days (4.2.2.5).

Store the laboratory method blank and laboratory control samples in amber glass jars with Teflon-lined lids at temperatures no higher than 4°C.

4.4   SAMPLE COLLECTION

Because of the complexity of this method, testers must be experienced with the test procedures in order to ensure reliable results.

4.4.1   Preliminary Field Determinations

Select the sampling site and the minimum number of sampling points according to ARB Method 1 or as specified by the Executive Officer.

Determine the stack pressure, temperature, and the range of velocity heads using ARB Method 2. Conduct a leak-check of the pitot lines according to ARB Method 2, Section 3.1.

Determine the moisture content using ARB Method 4 or its alternatives for the purpose of making isokinetic sampling rate settings.

Determine the stack gas dry molecular weight, as described in ARB Method 2, Section 3.6. If integrated sampling (ARB Method 3) is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. Do not change the nozzle size during the run. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of ARB Method 2).

Select a probe extension length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

The target sample volume and sampling time must already have been calculated for the source test protocol and approved by the end user as required by Sections 2.2 and 2.5. The total sampling time must be such that (1) the sampling time per point is not less than 2 minutes (or some greater time interval as specified by the Executive Officer), and (2) the total gas sample volume collected (corrected to standard conditions) will not be less than the target value calculated for the source test protocol (Section 2.5.5).

To avoid timekeeping errors, the number of minutes sampled at each point should be an integer or an integer plus one-half minute.

4.4.2   Preparation of Collection Train

Keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Caution: Do not use sealant greases in assembling the sampling train.

Record the performance of the setup procedures for the sampling train. Figure 10 is an example of a form for recording the sampling train setup data. The tester must record all of the routine information indicated on this form as well as any additional data which are necessary for documenting the quality of any reported results.

Place 100 ml of the impinger solution (4.2.5) in the first impinger and weigh. Record the total weight. Repeat the procedure for the second impinger. Leave the third impinger empty. Weigh the empty third impinger and record the weight.

Weigh 200 to 300 g of silica gel to the nearest 0.5 g directly into a tared impinger or silica gel cartridge just prior to assembly of the sampling train. The tester may optionally measure and record in advance of test time the weights of several portions of silica gel in air-tight containers.

One portion of the preweighed silica gel must then be transferred from its container to the silica gel cartridge or fourth impinger. Place the container in a clean place for later use in the sample recovery.

Using tweezers or clean disposable surgical gloves, place a filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly of the filter holder is completed.

Mark the probe extension with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

Assemble the train as in Figure 2. Place crushed ice around the impingers.

4.4.3   Leak-Check Procedures

4.4.3.1   Pretest Leak-Check

After the sampling train has been assembled, turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperature to stabilize. Leak-check the train at the sampling site by plugging the nozzle with a TFE plug and pulling a vacuum of at least 380 mm Hg (15 in. Hg).

Note: A lower vacuum may be used, provided that it is not exceeded during the test.

The following leak-check instructions for the sampling train are described in Section 4.1.4.1 of ARB Method 5. Start the pump with by-pass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the by-pass valve until the desired vacuum is reached. Do not reverse the direction of the by-pass valve. This will cause water to back up into the filter holder. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check as described below and start over.

Determine the leakage rate. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m^3 per min. (0.02 cfm), whichever is less, is unacceptable. Repeat the leak-check procedure until an acceptable leakage rate is obtained. Record the leakage rate on the field data sheet (Figure 5).

When the leak-check is completed, first slowly remove the plug from the inlet to the probe nozzle and immediately turn off the vacuum pump. This prevents water from being forced backward and keeps silica gel from being entrained backward.

4.4.3.2   Leak-Checks During Sample Run

If, during the sampling run, it becomes necessary to change a component (e.g., filter assembly or impinger), a leak-check shall be conducted immediately before the change is made. The leak-check shall be done according to the procedure described in Section 4.4.3.1 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than

0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either (1) record the leakage rate and correct the volume of gas sampled since the last leak-check as shown in Section 4.4.3.4 below, or (2) void the sampling run. Record the leakage rate.

Immediately after component changes, leak-checks must be conducted according to the procedure outlined in Section 4.4.3.1 above. Record the leakage rate on the field data sheet (Figure 5).

4.4.3.3 Post Test Leak-Check

A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done in accordance with the procedures outlined in Section 4.4.3.1 except that it shall be conducted at a vacuum equal to or greater than the maximum value recorded during the sampling run. Record the leakage rate on the field data sheet (Figure 5). If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either, (1) record the leakage rate and correct the sample volume as shown in Section 4.4.3.4 below, or (2) void the sampling run.

4.4.3.4 Correcting for Excessive Leakage Rates

If the leakage rate observed during any leak-check after the start of a test exceeds the maximum leakage rate L_a (see definition below), replace V_m in Equation 429-9 with the following expression:

$$V_m - \sum_{i=1}^{n} (L_i - L_a)\theta_i - (L_p - L_a)\theta_p \qquad \text{429-9}$$

Where:

V_m = Volume of gas sampled as measured by the dry gas meter (dscf).

L_a = Maximum acceptable leakage rate equal to 0.00057 m^3/min (0.02 ft^3/min) or 4% of the average sampling rate, whichever is smaller.

L_p = Leakage rate observed during the post-test leak-check, m^3/min (ft^3/min).

L_i = Leakage rate observed during the leak-check performed prior to the "ith" leakcheck (i = 1,2,3...n), m^3/min (ft^3/min).

θ_i = Sampling time interval between two successive leak-checks beginning with the interval between the first and second leak-checks, min.

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θ_p = Sampling time interval between the last (n^{th}) leak-check and the end of the test, min.

Substitute only for those leakage rates (L_i or L_p) which exceed L_a.

4.4.4 Train Operation

No smoking is allowed.

4.4.4.1 Sampling Train

During the sampling run maintain a sampling rate within 10 percent of true isokinetic, unless otherwise specified or approved by the Executive Officer. The actual sampling rate must be at or above the VSR (Equation 429-4) to collect the target sample mass in the estimated sampling time. If the target sampling rate cannot be achieved, adjust the planned sampling time to achieve the target sample volume (PSV).

For each run, record the data required on the sample data sheet shown in Figure 5. The operator must record the dry gas meter reading at the beginning of the test, at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted.

Record other readings required by Figure 5 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate.

Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

Clean the portholes prior to the test run to minimize the chance of sampling the deposited material. To begin sampling, remove the nozzle cap and verify that the pitot tube and probe extension are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream.

Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient (C_p) is 0.85 ± 0.02, and the stack gas equivalent density (dry molecular weight) (M_d) is equal to 29 ± 4. APTD-0576 (Reference 11.7) details the procedure for using the nomographs. If C_p and M_d are outside the above stated ranges, do not use the nomographs unless appropriate steps (see Reference 11.8) are taken to compensate for the deviations

When the stack is under significant negative pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe extension assembly into the stack to prevent water from being forced backward. If necessary, the pump may be turned on with the coarse adjust valve closed.

When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

Turn on the recirculating pump for the adsorbent module and the condenser, and begin monitoring the temperature of the gas entering the adsorbent trap. Ensure that the temperature of the gas is 20°C or lower before sampling is started.

Traverse the stack cross section, as required by ARB Method 1 or as specified by the Executive Officer, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe extension through the portholes. This minimizes the chance of extracting deposited material.

During the test run, take appropriate steps (e.g., adding crushed ice to the impinger ice bath) to maintain the temperature at the condenser outlet below 20°C (68°F). Also, periodically check the level and zero of the manometer.

If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced during a sample run. Another complete filter assembly must be used rather than changing the filter itself. Before a new filter assembly is installed, conduct a leak-check as outlined in Section 4.4.3.2. The total PAH analysis shall include the combined catches of all filter assemblies.

A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or, in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to approval by the Executive Officer.

Note that when two or more trains are used, a separate analysis of each train shall be performed, unless identical nozzle sizes were used on all trains, in which case the catches from the individual trains may be combined and a single analysis performed.

At the end of the sample run, turn off the pump, remove the probe extension assembly from the stack, and record the final dry gas meter reading. Perform a leak-check, as outlined in Section 4.4.3.3. Also, leak-check the pitot lines as described in ARB Method 2; the lines must pass this leak-check, in order to validate the velocity head data. Record leakage rates.

Record any unusual events during the sampling period.

4.4.4.2   Blank Train

There shall be at least one blank train for each series of three or fewer test runs. For those sources at which emissions are sampled at more than one sampling location, there shall be at least one blank train assembled at each location for each set of three or fewer runs. Prepare and set up the blank train in a manner identical to that described above for the sampling trains. The blank train shall be taken through all of the sampling train preparation steps including the leak-check without actual sampling of the gas stream. Recover the blank

train as described in Section 5.3. Follow all subsequent steps specified for the sampling train including extraction, analysis, and data reporting.

4.4.5   Calculation of Percent Isokinetic

Calculate percent isokinetic (Section 4.5.7) to determine whether the run should be repeated. If there was difficulty in maintaining isokinetic rates because of source conditions, consult with the Executive Officer for possible variance on the isokinetic rates.

4.5   CALCULATIONS

Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation.

4.5.1   Nomenclature

A = Cross-sectional area of stack, ft^2.

A_n = Cross-sectional area of nozzle, ft^2.

B_{ws} = Water vapor in the gas stream, proportion by volume.

C_s = Concentration of PAH in stack gas, ng/dscm, corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29.92 in. Hg) on dry basis.

G_s = Total mass of PAH in stack gas sample, ng.

ΔH = Average pressure differential across the orifice meter, mm H_2O (in. H_2O).

I = Percent isokinetic sampling.

L_a = Maximum acceptable leakage rate for either a pretest leak-check or for a leak-check following a component change; equal to 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.

L_i = Individual leakage rate observed during the leak-check conducted prior to the "ith" component change (i = 1, 2, 3, ...n), m^3/min (cfm).

L_p = Leakage rate observed during the post-test leak-check, m^3/min (cfm).

M_d = Molecular weight of stack gas, dry basis, lb/lb-mole (g/g-mole).

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

M_s = Molecular weight of stack gas, wet basis, lb/lb-mole (g/g-mole).
P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack gas pressure, mm Hg (in Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

Q_{std} = Dry volumetric stack gas flow rate corrected to standard conditions, dscf/min (dscm/min).

ρ_w = Density of water, 0.9982 g/mL (0.002201 lb/mL).

R = Ideal gas constant 0.06236 mm Hg-m³/°K-g-mole (21.83 in Hg-ft³/R-lb-mole).

T_m = Absolute average dry gas meter temperature, °K (°R).

T_s = Absolute average stack gas temperature °K (°R).

T_{std} = Standard absolute temperature, 293°K (528°R).

V_{lc} = Total volume of liquid collected in impingers and silica gel, mL.

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, dscm (dscf).

v_s = Stack gas velocity, calculated by ARB Method 2, Equation 2-9, ft/sec (m/sec).

Y = Dry gas meter calibration factor.

θ = Total sampling time, min.

θ_1 = Sampling time interval, from the beginning of a run until the first component change, min.

θ_i = Sampling time interval between two successive component changes, beginning with the interval between the first and second changes, min.

θ_p = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min.

φ_w = Sampling time interval, from the final (n^{th}) component change until

13.6 = Specific gravity of mercury.

60 = Conversion factor, sec/min.

100 = Conversion to percent.

4.5.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop

See sampling run record (Figure 5).

4.5.3 Dry Gas Volume

Use Equation 429-10 to correct the sample volume measured by the dry gas meter to standard conditions (20°C, 760 mm Hg or 68°F, 29.92 in Hg).

$$V_{m(std)} = V_m \, Y \, \frac{T_{std}}{T_m} \, \frac{\left(P_{bar} + \dfrac{\Delta H}{13.6}\right)}{P_{std}} = K_1 \, V_m \, Y \, \frac{\left(P_{bar} + \dfrac{\Delta H}{13.6}\right)}{T_m}$$
<div align="right">429-10</div>

Where:

$$K_1 = \frac{T_{std}}{P_{std}} = 0.3858 \, °K/mm \, Hg \text{ for metric units}$$

$$= 17.65 \, °R/in \, Hg \text{ for English units}$$

NOTE: Equation 429-10 may be used as written unless the leakage rate observed during any of the mandatory leak-checks (i.e., the post-test leak-check or leak-checks conducted prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, V_m in Equation 429-10 must be modified as described in Section 4.4.3.4.

4.5.4 Average Stack Gas Velocity

Calculate the average stack gas velocity, v_s, as specified in ARB Method 2, Section 5.2.

4.5.5 Volume of Water Vapor

Calculate the volume of water vapor using Equation 429-11 and the weight of the liquid collected during sampling (Sections 5.3.6 and 5.3.8).

$$V_{w(std)} = V_{lc} \, \frac{\rho_w}{M_w} \, \frac{RT_{std}}{P_{std}} = K_2 \, V_{lc}$$
<div align="right">429-11</div>

Where:

$$K_2 = 0.001333 \, m^3/mL \text{ for metric units, or}$$
$$= 0.04707 \, ft^3/mL \text{ for English units.}$$

4.5.6 Moisture Content

Calculate the moisture content of the gas, B_{ws}.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}}$$

429-12

NOTE: In saturated or water-droplet laden streams, the procedure for determining the moisture content is given in the note to Section 1.2 of Method 4. For the purpose of this method, the average stack-gas temperature from Figure 5 may be used for this determination, provided that the accuracy of the in-stack temperature sensor is $\pm 1^\circ C$ ($2^\circ F$)

4.5.7 Isokinetic Variation

4.5.7.1 Calculation from Raw Data

$$I = \frac{100\,T_s \left[K_3 V_{lc} + \dfrac{V_m Y}{T_m} \left(P_{bar} + \dfrac{\Delta H}{13.6} \right) \right]}{60\ \theta\ v_s\ P_s\ A_n}$$

429-13

Where:

$$K_3 = 0.003454 \text{ mm Hg-m}^3/\text{mL-}^\circ K \text{ for metric units}$$

$$= 0.002669 \text{ in Hg-ft}^3/\text{mL-}^\circ R \text{ for English units}$$

4.5.7.2 Calculation from Intermediate Values

$$I = \frac{100\,T_s\ V_{m(std)}\ P_{std}}{T_{std}\ v_s\ \theta\ A_n\ P_s\ 60\ (1 - B_{ws})}$$

$$= K_4 \frac{T_s\ V_{m(std)}}{P_s\ v_s\ \theta\ A_n\ (1 - B_{ws})}$$

429-14

Where:

$$K_4 = 4.320 \text{ for metric units.}$$

$$= 0.09450 \text{ for English units.}$$

4.5.8   Average stack gas dry volumetric flow rate

Use Equation 429-15 to calculate the average dry volumetric flow rate of the gas.

$$Q_{std} = 60 \ K_1 \ (1 - B_{ws}) \ v_s \ A \left(\frac{P_s}{T_s} \right) \qquad \text{429-15}$$

Where:

$$K_1 = \frac{T_{std}}{P_{std}} = 0.3858 \text{ °K/mm Hg for metric units}$$

$$= 17.65 \text{ °R/in Hg for English units}$$

4.6   ISOKINETIC CRITERIA

If 90 percent < I < 110 percent, the isokinetic results are acceptable. If there is a bias to the results because I < 90 percent or I > 110 percent, then the results must be rejected and the test repeated, unless the test results are accepted by the Executive Officer.

5   SAMPLE RECOVERY

5.1   SAMPLE RECOVERY APPARATUS

5.1.1   Probe Nozzle Brush

Teflon brush with Teflon handle. The brush shall be properly sized and shaped to brush out the probe nozzle.

5.1.2   Wash Bottles

Teflon wash bottles are required; Teflon FEP®.

5.1.3   Glass Sample Storage Containers

Precleaned narrow mouth amber glass bottles, 500 mL or 1000 mL. Screw cap liners shall be Teflon.

5.1.4   Filter Storage Containers

Sealed filter holder or precleaned, wide-mouth amber glass containers with Teflon-lined screw caps.

5.1.5   Balance

To measure condensed water to within 0.5 g.

5.1.6   Silica Gel Storage Containers

Air tight metal containers to store silica gel.

5.1.7   Funnel and Rubber Policeman

To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

5.1.8   Funnel

To aid in sample recovery. Glass or Teflon® must be used.

5.1.9   Ground Glass Caps or Hexane Rinsed Aluminum Foil

To cap off adsorbent tube and the other sample-exposed portions of the aluminum foil.

5.1.10 Aluminum Foil

Heavy-duty, precleaned with methylene chloride.

5.2   SAMPLE RECOVERY REAGENTS

5.2.1   Reagent Water

Deionized (DI), then glass distilled, and stored in hexane and methylene chloride-rinsed glass containers with TFE-lined screw caps.

5.2.2   Acetone

Nanograde quality. "Distilled in Glass" or equivalent, stored in original containers. A blank must be screened by the analytical detection method.

5.2.3   Hexane

Nanograde quality. "Distilled in Glass" or equivalent, stored in original containers. A blank must be screened by the analytical detection method.

5.2.4   Methylene Chloride

Nanograde quality or equivalent. A blank must be screened by the analytical detection method.

5.3   SAMPLE RECOVERY PROCEDURE

No smoking is allowed.

Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period and a post test leak-check has been performed (4.4.3.3). Allow the probe to cool.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle. Conduct the post test leak-check as described in Section 4.4.3.3. Remove the probe from the train and close off both ends of the probe with precleaned aluminum foil (5.1.10). Seal off the inlet to the train with a ground glass cup or precleaned aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area must be clean, and enclosed so that the chances of contaminating the sample will be minimized.

Inspect the train prior to and during disassembly and note any abnormal conditions, broken filters, color of the impinger liquid, etc. Figure 6 summarizes the recovery procedure described in Sections 5.3.1 to 5.3.8.

Figure 11 is an example of a form for recording the performance of the sample recovery procedure. The tester must record all of the routine information indicated on this form as well as any additional data which are necessary for documenting the quality of any reported results.

5.3.1   Sample Container No. 1 (front half rinses)

Quantitatively recover material deposited in the nozzle, probe, the front half of the filter holder, and the cyclone, if used, first by brushing and then by sequentially rinsing with acetone, hexane, and methylene chloride three times each. Place all these rinses in Container No. 1. Mark the liquid level.

5.3.2   Cyclone Catch

If the optional cyclone is used, quantitatively recover the particulate matter by sequentially rinsing the cyclone with acetone, hexane, and methylene chloride. Store in a clean sample container and cap.

5.3.3   Sample Container No. 2 (filter)

Carefully remove the filter from the filter holder and place it in its identified container. Use a pair of precleaned tweezers to handle the filter. Do not wrap the filter in aluminum foil. If it is necessary to fold the filter, make sure that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and/or filter fibers which adhere to the filter holder gasket by using a dry inert bristle brush and/or a sharp-edged blade. Seal the container.

5.3.4   Sorbent Module

Remove the sorbent module from the train and cap it.

5.3.5   Sample Container No. 3 (back half rinses)

Rinse the back half of the filter holder, the transfer line between the filter and the condenser, and the condenser (if using the separate condenser-sorbent trap) three times each with acetone, hexane and methylene chloride, and collect all rinses in Container No. 3. If using the combined condenser/sorbent trap, the rinse of the condenser shall be performed in the laboratory after removal of the XAD-2 portion. If the optional water knockout trap has been employed, the contents and rinses shall be placed in Container No. 3. Rinse it three times each with acetone, hexane, and methylene chloride. Mark the liquid level.

The back half rinses may also be combined in a single container with the front half rinses (Section 5.3.1).

5.3.6   Sample Container No. 4 (Impinger contents)

Wipe off the outside of each of the first three impingers to remove excess water and other material. Weigh the impingers and contents to the nearest ±0.5 g using a balance. Record the weight. Calculate and then record the weight of liquid collected during sampling. Use this weight and the weight of liquid collected in the silica gel (Section 5.3.8) to calculate the moisture content of the effluent gas (Sections 4.5.5 and 4.5.6). Pour the impinger catch directly into Container No. 4. Mark the liquid level.

5.3.7   Sample Container No. 5 (Impinger rinses)

Rinse each impinger sequentially three times with acetone, hexane, and methylene chloride and pour rinses into Container No. 5. Mark the liquid level. These rinses may be combined with the previously weighed impinger contents in Container No. 4.

5.3.8   Weighing Silica Gel

Weigh the spent silica gel to the nearest 0.5 g using a balance. Record the weight. Calculate and then record the weight of liquid collected during sampling. Use this weight and the weight of liquid collected in the impingers (Section 5.3.6) to calculate the moisture content of the effluent gas (Sections 4.5.5 and 4.5.6). .

5.4   SAMPLE PRESERVATION AND HANDLING

From the time of collection to extraction, maintain all samples (Sections 5.3.1 to 5.3.7) at 4°C or lower and protect from light. All samples must be extracted as soon as practically feasible, but within 21 days of collection; and all extracts must be analyzed as soon as practically feasible, but within 40 days of extraction. Success in meeting the holding time requirement will depend on pre-test planning by the tester and the laboratory.

6 ANALYTICAL PREPARATION

This method is restricted to use only by or under the supervision of analysts experienced in the use of capillary column gas chromatography/mass spectrometry and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedures described in Sections 7.3, 8.2.6, and 8.3.1.

6.1 SAFETY

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Nevertheless, each chemical compound should be treated as a potential health hazard and exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis. Reference 11.9 describes procedures for handling hazardous chemicals in laboratories.

The following method analytes have been classified as known or suspected human or mammalian carcinogens: benzo(a)anthracene and dibenzo- (a,h,)anthracene. A guideline for the safe handling of carcinogens can be found in Section 5209 of Title 8 of the California Administrative Code.

6.2 CLEANING OF LABORATORY GLASSWARE

Glassware used in the analytical procedures (including the Soxhlet apparatus and disposable bottles) must be cleaned as soon as possible after use by rinsing with the last solvent used in it. This must be followed by detergent washing with hot water, and rinses with tap water, deionized water, acetone, hexane, and methylene chloride. Other cleaning procedures may be used as long as acceptable blanks are obtained. Acceptance criteria for blanks are given in Section 8.2.

Clean aluminum foil with acetone followed by hexane and methylene chloride.

6.3 APPARATUS

6.3.i Grab Sample Bottle

Amber glass, 125-mL and 250-mL, fitted with screw caps lined with Teflon. The bottle and cap liner must be acid washed and solvent rinsed with acetone and methylene chloride, and dried before use.

6.3.2 Concentrator Tube, Kuderna-Danish

10-mL, graduated (Kontes-K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. A ground glass stopper must be used to prevent evaporation of extracts.

6.3.3 Evaporation Flask, Kuderna-Danish

500-mL (Kontes K-570001-0500 or equivalent). (Attached to concentrator tube with springs).

6.3.4   Snyder Column, Kuderna-Danish

Three-ball macro (Kontes K-569001-0121 or equivalent).

6.3.5   Snyder Column, Kuderna-Danish

Two-ball micro (Kontes K-569001-0219 or equivalent).

6.3.6   Minivials

1.0 mL vials; cone-shaped to facilitate removal of very small samples; heavy wall borosilicate glass; with Teflon-faced rubber septa and screw caps.

6.3.7   Soxhlet Apparatus

1 liter receiver, 1 heating mantle, condenser, Soxhlet extractor.

6.3.8   Rotary Evaporator

Rotovap R (or equivalent), Brinkmann Instruments, Westbury, NY.

6.3.9   Nitrogen Blowdown Apparatus

N-Evap Analytical Evaporator Model 111 (or equivalent), Organomation Associates Inc., Northborough, MA.

6.3.10   Analytical Balance

Analytical. Capable of accurately weighing to the nearest 0.0001 g.

6.3.11   Disposable Pipet

5 3/4 inch x 7.0 mm OD.,

6.4   SAMPLE PREPARATION REAGENTS

6.4.1   Reagent water

Same as 5.2.1.

6.4.2   Acetone

Same as 5.2.2.

6.4.3   Hexane

Same as 5.2.3.

6.4.4   Methylene Chloride

Same as 5.2.4.

6.4.5   Sulfuric Acid

ACS. Reagent grade. Concentrated, sp. gr. 1.84.

6.4.6   Sodium Sulfate

ACS. Reagent grade. Granular, anhydrous. Purify prior to use by extracting with methylene chloride and oven drying for 4 or more hours in a shallow tray. Place the cleaned material in a glass container with a Teflon-lined screw cap, and store in a desiccator.

6.4.7   Silica Gel

For column chromatography, type 60, EM reagent, 100-200 mesh, or equivalent. Soxhlet extract with methylene chloride, and activate by heating in a foil covered glass container for longer than 16 hours at 130 °C, then store in a desiccator. The storage period shall not exceed two days.

NOTE: The performance of silica gel in the column cleanup procedure varies with manufacturers and with the method of storage. The analyst shall establish a procedure that satisfies the performance criteria of Section 6.6.1.

6.4.8   Alumina: Acidic

Soxhlet extract with methylene chloride, and activate in a foil covered glass container for 24 hours at 190 °C.

NOTE: The performance of alumina in the column cleanup procedure varies with manufacturers and with the method of storage. The analyst shall establish a procedure that meets the performance criteria of Section 6.6.1.

6.4.9   Nitrogen

Obtained from bleed from liquid nitrogen tank.

6.5   SAMPLE EXTRACTION

WARNING: Stack sampling will yield both liquid and solid samples for PAH analysis. Samples must not be split prior to extraction even when they appear homogeneous as in the case of single liquid phase samples. Solid samples such as the resin are not homogeneous and particulate matter may not be uniformly distributed on the filter. In addition, filter samples are generally so small that the desired detection limit might not be achieved if the sample were split.

The recovered samples may be combined as follows:

1) Particulate filter and particulate matter collected on the filter (Section 5.3.3), cyclone catch (Section 5.3.2) and sample container No. 1 (Section 5.3.1).

2) Sample container No. 3 (Section 5.3.5), resin (Section 5.3.4) and rinse of resin cartridge.

3) Sample container No.4 (Section 5.3.6) and sample container No.5 (Section 5.3.7)

Two schemes for sample preparation are described in Sections 6.5.1 and 6.5.2 below. One of these must be used.

Section 6.5.1 describes sample preparation procedures for separate GC/MS analyses of impingers and the remainder of the sampling train. Figure 7 is a flowchart of the extraction and cleanup procedures.

Section 6.5.2 describes sample preparation procedures for GC/MS analysis of a single composite extract from each sampling train. The recovered samples are combined as shown in Figure 8.

6.5.1   Separate Analysis of Impingers

A separate analysis of the impingers can be used to determine whether there has been breakthrough of PAHs past the resin.

6.5.1.1   Extraction of Liquid Samples

A. Sample Container No. 1 (Front half rinses)

Concentrate the contents of sample container No. 1 (Section 5.3.1) to a volume of about 1-5 mL using the nitrogen blowdown apparatus. Rinse the sample container three times with small amounts of methylene chloride and add these rinses to the concentrated solution. Concentrate further to about 1-5 mL. This residue will likely contain particulate matter which was removed in the rinses of the probe and nozzle. Transfer the residue (along with three rinses of the final sample vessel) to the Soxhlet apparatus with the filter and particulate catch and proceed as described under Section 6.5.1.2 below.

B. Sample Container No. 3 (Back half rinses)

Concentrate the contents of sample container No. 3 (Section 5.3.5) to a volume of about 1-5 mL using the nitrogen blowdown apparatus. Rinse the sample container three times with small amounts of methylene chloride and add these rinses to the concentrated solution. Concentrate further to about 1-5 mL. Combine this residue (along with three rinses of the final sample vessel) in the Soxhlet apparatus with the resin sample, and proceed as described under Section 6.5.1.2 below.

C. Containers No. 4 and No. 5 (Impinger contents and rinses)

Place the contents of Sample Containers No. 4 and No. 5 (Sections 5.4.6 and 5.4.7) in a separatory funnel. Add the appropriate amount of ^{2}H-labelled alternate standard solution (Section 7 and Table 7 or 7A) to achieve the final extract concentrations indicated in Table 8 or 8A. The amounts required by Section 7.2.4 are based on a final volume of 500 μL for analysis (450 μL of sample extract and 50 μL of recovery standard solution). Extract the sample three times with 60 mL aliquots of methylene chloride. Combine the organic fractions. Divide the extract in two: one half to be archived, and the other for cleanup and GC/MS analysis. Store the archive sample at 4°C away from light.

Pour the remaining extract through Na_2SO_4 into a round bottom flask. Add 60 to 100 mL hexane and evaporate to about 10 mL. Repeat three times or less if the methylene chloride can be removed with less hexane. Add the appropriate amount of alternate standard (Section 7.2.7) to achieve the final extract concentrations shown in Table 6 or 6A. This standard must be used to monitor the efficiency of the cleanup procedure.

Concentrate the remaining sample to 2 mL with a Kuderna-Danish concentrator or rotary evaporator, then transfer the extract to a 8 mL test tube with hexane. Proceed with sample cleanup procedures below (Section 6.6).

6.5.1.2   Extraction of Solid Samples

Filter, Particulate matter, and Resin

The Soxhlet apparatus must be large enough to allow extraction of the sample in a single batch. Clean the Soxhlet apparatus by a 4 to 8 hr Soxhlet with methylene chloride at a cycling rate of 3 cycles per hour. Discard the solvent. Add 20 g Na_2SO_4 to the thimble. Combine the filter, resin, glass wool, and concentrated front and back half rinses (6.5.1.1A and 6.5.1.1B) and place on top of the Na_2SO_4. Add the appropriate amount of internal standard (Section 7.2.4 and Table 7) to achieve the final extract concentrations indicated in Table 8.

Place the thimble in the Soxhlet apparatus, and add about 700 mL of methylene chloride to the receiver. Assemble the Soxhlet, turn on the heating controls and cooling water, and allow to reflux for 16 hours at a rate of 3 cycles per hour. After extraction, allow the Soxhlet to cool. Divide the sample in two: one half to be archived, and the other for cleanup and GC/MS analysis. Store the archive sample at 4°C away from light.

Exchange the remaining extract to hexane. Add 60 to 100 mL hexane and evaporate to about 10 mL. Repeat three times or as necessary to remove the methylene chloride. Add the appropriate amount of alternate standard (Section 7.2.7 and Table 7 or 7A) to achieve the final extract concentrations shown in Table 8 or 8A. This alternate standard must be used to monitor the efficiency of the cleanup procedure when the impingers are analyzed separately from the remainder of the sampling train.

Concentrate the remaining sample to about 2 mL with a Kuderna-Danish concentrator or rotoevaporator, then transfer the extract to a 8-mL test tube with hexane. Proceed with sample cleanup procedures below (Section 6.6).

6.5.2   Single Composite Extract For Analysis

6.5.2.1   Extraction of Aqueous Samples

Containers No. 4 and No. 5 (Impinger contents and rinses)

Pour the contents of Sample Containers No. 4 and No. 5 (Sections 5.3.6 and 5.3.7) into an appropriate size separatory funnel. Do not add internal standards. Instead, add the appropriate amount of alternate standard spiking solution (Section 7 and Table 7 or 7A) to achieve the final extract concentrations indicated in Table 8 or 8A.

Extract the sample three times with 60 mL aliquots of methylene chloride. Combine the organic fractions with the solid samples and concentrated rinses (6.5.2.2) in a Soxhlet extractor.

6.5.2.2   Extraction of Solid Samples

Concentrate the front and back half rinses as described in Sections 6.5.1.1A and 6.5.1.1B. Clean the Soxhlet apparatus as in Section 6.5.1.2. Place the filter and resin in the Soxhlet apparatus along with the concentrated front and back half rinses and the impinger extract. Add the internal standards, extract the sample, and concentrate the extract as described in Section 6.5.1.2. Divide the extract into two equal portions. Store one of these, the archive sample, at 4 °C away from light. The remaining extract must be exchanged to hexane as described in Section 6.5.1.2. Do not add the alternate standard to this composite extract. It has already been added to the impinger sample (6.5.2.1).

Concentrate the extract to 2 mL with a Kuderna-Danish concentrator or rotary evaporator, then transfer to a 8-mL test tube with hexane or equivalent non-polar solvent such as isooctane. Proceed with sample cleanup procedures below (Section 6.6)

6.6   COLUMN CLEANUP

Several column chromatographic cleanup options are available. Either of the two described below may be sufficient. Before using a procedure for the cleanup of sample extracts, the analyst must demonstrate that the requirements of Sections 8.1.3.1 and 8.2.6 can be met using the cleanup procedure. Acceptable alternative cleanup procedures may also be used provided that the analyst can demonstrate that the performance requirements of Sections 8.1.3.1 and 8.2.6 can be met. Compliance with the requirements of Sections 8.1.1.1 and 8.2.6 must also be demonstrated whenever there is a change in the column cleanup procedure used for the initial demonstration.

The sample extract obtained as described in Sections 6.5.1C and 6.5.1.2 or 6.5.2.2 is concentrated to a volume of about 1 mL using the nitrogen blowdown apparatus, and this is transferred quantitatively with hexane rinsings to at least one of the columns described below.

6.6.1   Column Preparation

A. Silica Gel Column

Pack a glass gravity column (250 mm x 10 mm) in the following manner:

Insert a clean glass wool plug (Section 4.2.7) into the bottom of the column and add 10 grams of activated silica gel (Section 6.4.7) in methylene chloride. Tap the column to settle the silica gel, and then add a 1 cm layer of anhydrous sodium sulfate (Section 6.4.6)

Variations among batches of silica gel may affect the elution volume of the various PAH. Therefore, the volume of solvent required to completely elute all of the PAH must be verified by the analyst. The weight of the silica gel can then be adjusted accordingly. Satisfactory recovery (as defined in Section 6.6) of each native PAH in the LCS (8.1.3) must be demonstrated whenever there is a change in the method of preparing the silica gel columns.

B. Acid Alumina Column

Pack a 250 mm x 10 mm glass gravity column as follows:

Insert a clean glass wool plug (Section 4.2.7) into the bottom of the column. Add 6 g of acid alumina prepared as described in Section 6.4.8. Tap the column gently to settle the alumina. and add 1 cm of anhydrous sodium sulfate to the top.

Satisfactory recovery (as defined in Section 6.6) of each native PAH in the LCS (8.1.3) must be demonstrated whenever there is a change in the method of preparing the acid alumina columns.

6.6.2   Column Chromatography Procedure

A. Silica Gel Column

Elute the column with 40 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 1 mL sample extract onto the column using two additional 2 mL rinses of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, begin elution of the column with 25 mL of hexane followed by 25 mL of methylene chloride/hexane (2:3)(v/v). Collect the entire eluate. Concentrate the collected fraction to about 5 mL using the K-D apparatus or a rotary evaporator. Do not allow the extract to go to dryness.

Transfer to a minivial using a hexane rinse and concentrate to 450 µL using a gentle stream of nitrogen. Store the extracts in a refrigerator at 4 °C or lower away from light until GC/MS analysis (Section 7).

B. Alumina Column

Elute the column with 50 mL of hexane. Let the solvent flow through the column until the head of the liquid in the column is just above the sodium sulfate layer. Close the stopcock to stop solvent flow. .'

Transfer 1 mL of the sample extract onto the column. Rinse out extract vial with two 1 mL rinses of hexane and add it to the top of the column immediately. To avoid overloading the column, it is suggested that no more than 300 mg of extractable organics be placed on the column.

Just prior to exposure of the sodium sulfate to the air, elute the column with a total of 15 mL of hexane. If the extract is in 1 mL of hexane, and if 2 mL of hexane was used as a rinse, then 12 mL of additional hexane should be used. Collect the effluent and concentrate to about 2 mL using the K-D apparatus or a rotary evaporator.

Transfer to a minivial using a hexane rinse and concentrate to 450 µL using a gentle stream of nitrogen. Store the extracts at 4°C or lower away from light until GC/MS analysis.

7   GC/MS ANALYSIS

7.1   APPARATUS

7.1.1   Gas Chromatograph

An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The GC injection port must be designed for capillary columns. Splitless injection is recommended.

7.1.2   Column

Fused silica columns are required.

A. 30 M long x 0.32 mm ID fused silica capillary column coated with a crosslinked phenyl methyl silicone such as DB-5.

B. Any column equivalent to the DB-5 column may be used as long as it has the same separation capabilities as the DB-5.

7.1.3   Mass Spectrometer

7.1.3.1   Low Resolution

A low resolution mass spectrometer (LRMS) equipped with a 70 eV (nominal) ion source operated in the electron impact ionization mode, and capable of monitoring all of the ions in each Selected Ion Monitoring (SIM) group (Table 13) with a total cycle time of 1 second or less.

7.1.3.2 High Resolution

The high resolution mass spectrometer (HRMS) must be capable of operation in the SIM mode at a resolving power of 8,000. Electron impact ionization must be used. The mass spectrometer must be capable of monitoring all of the ions listed in each of the three SIM descriptors (Table 14) with a total cycle time of 1 second or less.

7.1.4 GC/MS Interface

Any gas chromatograph to mass spectrometer interface may be used as long as it gives acceptable calibration response for each analyte of interest at the desired concentration and achieves the required tuning performance criteria (Sections 7.3.5 and 7.3.6). All components of the interface must be glass or glass-lined materials. To achieve maximum sensitivity, the exit end of the capillary column should be placed in the mass spectrometer ion source without being exposed to the ionizing electron beam.

7.1.5 Data Acquisition System

A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all data obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and plot a Selected Ion Current Profile or SICP (a plot of the abundances of the selected ions versus time or scan number). Software must also be able to integrate, in any SICP, the abundance between specified time or scan-number limits.

The data system must provide hard copies of individual ion chromatograms for selected gas chromatographic time intervals.

The data system must also be able to provide hard copies of a summary report of the results of the GC/MS runs. Figures 14A to 14C show the minimum data that the system must be available to provide.

7.2 REAGENTS

7.2.1 Stock Standard Solution (1.00 µg/µL)

Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

7.2.2 Preparation of Stock Solutions

A. Calibration standards. Prepare stock calibration standard solutions of each of the PAH analytes by accurately weighing the required amount of pure material. Dissolve the material in isooctane and dilute to volume. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

B. Internal standards. Prepare stock solutions in isooctane of the fourteen internal standards listed in Table 4 or 4A at concentrations of 1000 ng/μL.

C. Recovery standards. Prepare stock solutions in isooctane of the three recovery standards listed in Table 4 or 4A at concentrations of 1000 ng/μL.

D. Alternate standard. Prepare a stock solution in isooctane of the alternate standard listed in Table 4 or 4A at a concentration of 1000 ng/μL.

E. Surrogate standards. Prepare stock solutions in isooctane of the surrogate standards listed in Table 4 or 4A at a concentration of 1000 ng/μL.

Store stock standard solutions in Teflon®-sealed screw-cap bottles at 4°C and protect from light. Stock standard solutions must be checked frequently for signs of degradation or evaporation, especially just before using them to prepare calibration standard solutions or spiking solutions.

Replace stock standard solutions every 12 months or more frequently if comparison with quality control check samples according to Section 7.4.1 indicates a problem.

7.2.3   Calibration Standards

Prepare calibration standards at a minimum of five concentration levels. One of the calibration standards should be at a concentration near, but above, the method detection limit. The others should include the range of concentrations found in real samples but should not exceed the linear range of the GC/MS system.

Prepare calibration working standard solutions by combining appropriate volumes of individual or mixed calibration standards with internal standard, recovery standards, and alternate standard spiking solution and making up to volume with hexane to obtain the solution concentrations given in Tables 5, 6, and 6A. The suggested ranges are 0.25 ng/μL to 5.0 ng/μL for LRMS and 10 pg/μL to 500 pg/μL for HRMS.

All standards must be stored at 4°C or lower and must be freshly prepared if the check according to Section 7.4.1 indicates a problem.

7.2.4   Internal Standard (IS) Spiking Solution

The concentration of internal standard in the IS spiking solution must be such that the amount of solution added to the calibration standard solution and the sample is at least 2 mL.

Prepare the internal standard spiking solution by using appropriate volumes of stock solutions of Section 7.2.2B to give the concentrations shown in Table 4 or 4A. A volume of 2 mL of either the LRMS or HRMS spiking solution will provide the amount of the internal standards that must be added to the sample (Table 7 or 7A) before extraction to achieve, in a final volume of

500 µL, the sample extract concentrations shown in Table 8 for LRMS and Table 8 or 8A for HRMS analysis. The target concentrations in Tables 8 and 8A are based on a final volume of 500 µL and 100 percent recovery of the internal standards added to the sample.

7.2.5   Recovery Standard Spiking Solution

The concentration of recovery standard in this spiking solution must be such that the amount of solution added to the concentrated sample extract is 50 µL to give a final extract volume of 500 µL.

Use an appropriate volume of stock solution of Section 7.2.2C to prepare a recovery standard spiking solution with the concentrations shown in Table 4 or 4A. Store at 4 °C or lower.

A volume of 50 µL of the recovery standard spiking solution shown in Table 4 or 4A will provide the amount of each recovery standard required by Table 7 or 7A to achieve the target sample concentration of Table 8 or 8A. Final volumes, may be adjusted depending on the target detection limit.

7.2.6   Surrogate Standard Spiking Solution

The concentration of surrogate standard in this spiking solution must be such that the amount of solution added to the calibration standard solution and the sorbent module is at least 2 mL.

Prepare the surrogate standard spiking solution by using the appropriate volume of stock solution of Section 7.2.2E to give the concentration shown in Table 4 or 4A. A volume of 2 mL of either the LRMS or HRMS spiking solution will provide the amount of the surrogate standards that must be added to the sample (Table 7 or 7A) before sampling to achieve the sample extract concentrations shown in Table 8 or 8A in a final sample volume of 500 µL.

7.2.7   Alternate Standard Spiking Solution

The concentration of alternate standard in this spiking solution must be such that the amount of solution added to the calibration standard solution and the sample extracts is at least 2 mL.

Prepare the alternate standard spiking solution by using the appropriate volume of stock solution of Section 7.2.2D to give the concentration shown in Table 4 or 4A. A volume of 2 mL of either the LRMS or HRMS spiking solution will provide the amount of the alternate standard that must be added to the sample (Table 7 or 7A) before extraction to achieve the sample extract concentrations shown in Table 8 or 8A in a final sample volume of 500 µL.

7.2.8   Calibration Check Standard

The calibration check standard shall be used for column performance checks, and for continuing calibration checks. Solution #3 from Table 5 shall be the calibration check standard for LRMS, while Solution #3 from Table 6 or 6A shall be the calibration check standard for HRMS.

7.3 INITIAL CALIBRATION

An acceptable initial calibration (7.3.8) is required before any samples are analyzed, and then intermittently throughout sample analyses as dictated by results of the continuing calibration procedures described in Section 7.4. The GC/MS system must be properly calibrated and the performance documented during the initial calibration.

7.3.1 Retention Time Windows

Before sample analysis, determine the retention time windows during which the selected ions will be monitored. Determine Relative Retention Time (RRTs) for each analyte by using the corresponding ^2H - labelled standard.

7.3.2 GC Operating Conditions

The GC column performance (Section 7.3.5) must be documented during the initial calibration. Table 10 summarizes GC operating conditions known to produce acceptable results with the column listed. The GC conditions must be established by each analyst for the particular instrumentation by injecting aliquots of the calibration check standard (7.2.8). It may be necessary to adjust the operating conditions slightly based on observations from analysis of these solutions. Other columns and/or conditions may be used as long as column performance criteria of Section 7.3.5 are satisfied.

Thereafter the calibration check standard must be analyzed daily to verify the performance of the system (Section 7.4).

7.3.3 GC/MS Tuning Criteria

A. Low Resolution Mass Spectrometry

Use a compound such perfluorotributylamine (PFTBA) to verify that the intensity of the peaks is acceptable. If PFTBA is used, mass spectral peak profiles for m/z 69, 219 and 264 must be recorded, plotted, and reported. The scan should include a minimum of +/- two peaks (i.e, m/z 67-71 for the m/z 69 profile).

B. High Resolution Mass Spectrometry

Tune the instrument to meet the minimum required resolving power of 8,000 at 192.9888 or any other PFK reference signal close to 128.0626 (naphthalene). Use peak matching and the chosen PFK reference peak to verify that the exact mass of m/z 242.9856 is within 5 ppm of the required value. The selection of the low and high mass ions must be such that they provide the largest voltage jump performed in any of the three mass descriptors.

7.3.4   MS Operating Conditions

A. Low Resolution Mass Spectrometry

Analyze standards and samples with the mass spectrometer operating in the Selected Ion Monitoring (SIM) mode with a total cycle time of 1 second or less.

B. High Resolution Mass Spectrometry

Analyze standards and samples with the mass spectrometer operating in the SIM mode with a total cycle time (including the voltage reset time) of one second or less.

A reference compound such as Perfluorokerosene (PFK) must be used to calibrate the SIM mass range. One PFK ion per mass descriptor is used as a lock-mass ion to correct for mass drifts that occur during the analysis. In addition to the lock-mass ion, several ions characteristic of PFK are monitored as QC check ions (Table 13).

7.3.5   GC Column Performance Criteria

A.   The height of the valley between anthracene and phenanthrene at m/z 178 or the ^{2}H-analogs at m/z 188 shall not exceed 50 percent of the taller of the two peaks.

B.   The height of the valley between benzo(b)fluoranthene and benzo(k)fluoranthene shall not exceed 60 percent of the taller of the two peaks.

If these criteria are not met and normal column maintenance procedures are not successful, the column must be replaced and the initial calibration repeated.

7.3.6   Mass Spectrometer Performance

A. Low Resolution Mass Spectrometry

Verify acceptable sensitivity during initial calibration. Demonstrate that the instrument will achieve a minimum signal-to-noise ratio of 10:1 for the quantitation and confirmation ions when the calibration standard with the lowest concentration is injected into the GC/MS system.

B. High Resolution Mass Spectrometry

Record the peak profile of the high mass reference signal (m/z 242.9856) obtained during peak matching by using the low-mass PFK ion at m/z 192.9888 (or lower in mass) as a reference. The minimum resolving power of 8,000 must be demonstrated on the high-mass ion while it is transmitted at a lower accelerating voltage than the low-mass reference ion, which is transmitted at full sensitivity.

The format of the peak profile representation must allow manual determination of the resolution, that is, the horizontal axis must be a calibrated mass scale (amu or ppm per division).

The peak width of the high mass ion at 5 percent of the peak height must not exceed 125 ppm in mass.

7.3.7   Calibration Procedure

Using stock standards, prepare at least five calibration standard solutions, using the same solvent that was used in the final sample extract. Keep the recovery standards and the internal standards at fixed concentrations. Adjust the concentrations recommended in Tables 5 and 6, if necessary, to ensure that the sample analyte concentration falls within the calibration range. The calibration curve must be described within the linear range of the method.

Calibrate the mass spectrometer response using a 2 µL aliquot of each calibration solution. Analyze each solution once.

Calculate:

        A.   the relative response factors (RRFs) for each analyte as described in Sections 7.7.1.1, 7.7.1.2, and 7.7.1.3.

        B.   the mean RRFs as required by Section 7.7.1.4.

        C.   the standard deviation (SD) and relative standard deviation (RSD) as required by Section 7.7.2.

Report all results as required by Section 10.2.

7.3.8   Criteria for Acceptable Initial Calibration

An acceptable initial calibration must satisfy the following performance criteria:

A. The requirements of Sections 7.3.5 and 7.4.6 must be met.

B. The signal to noise ratio (S/N) for the GC signals present in every selected ion current profile (SICP) must be > 10:1 for the labelled standards and unlabelled analytes.

C. The percent relative standard deviation for the mean relative response factors must be no greater than 30 percent for both the unlabelled analytes and internal standards (Section 7.7.2). Otherwise, take corrective action as required by Section 7.7.2.

7.4   CONTINUING CALIBRATION

The continuing calibration consists of an analysis of the calibration check standard (Section 7.2.8) once during each 12-hour shift as described in Section 7.4.1.

The criteria for acceptable continuing calibration are given in Section 7.4.2. These must be satisfied or else corrective action must be taken as required by Section 7.4.2.

7.4.1   Calibration Check

The calibration check standard (Section 7.2.8) must be analyzed at the beginning and end of each analysis period, or at the beginning of every 12-hour shift if the laboratory operates during consecutive 12 hour shifts.

Inject a 2-μL aliquot of the calibration check standard (Section 7.2.8) into the GC/MS. Use the same data acquisition parameters as those used during the initial calibration.

Check the retention time windows for each of the compounds. They must satisfy the criterion of Section 7.4.2C

Check for GC resolution and peak shape. Document acceptable column performance as described in Section 7.3.5. If these criteria are not met, and normal column maintenance procedures are unsuccessful, the column must be replaced and the calibration repeated.

Calculate the continuing RRF and ΔRRF, the relative percent difference (RPD) between the daily RRF and the initial calibration mean RRF as described in Section 7.7.1.5.

Report the results as required by Section 10.2.

7.4.2   Continuing Calibration Performance Criteria

An acceptable continuing calibration must satisfy the following performance criteria:

A. The signal to noise ratio (S/N) for the GC signals present in the selected ion current profile (SICP) for all labelled and unlabelled standards must be ≥ 10:1.

B. The measured RRFs of all analytes (labelled and unlabelled) must be within 30 percent of the mean values established during the initial calibration. If this criterion is not satisfied, a new initial calibration curve must be established before sample extracts can be analyzed.

C. The retention time for any internal standard must not change by more than 30 seconds from the most recent calibration check. Otherwise, inspect the chromatographic system for malfunctions and make the necessary corrections. Document acceptable performance with a new initial calibration curve.

7.5   GC/MS ANALYSIS

The laboratory may proceed with the analysis of samples and blanks only after demonstrating acceptable performance as specified in Sections 7.3 and 7.4.

Analyze standards, field samples and QA samples (Section 8.1) with the gas chromatograph and mass spectrometer operating under the conditions recommended in Sections 7.3.2 and 7.3.4.

Approximately 1 hr before HRGC/LRMS or HRGC/HRMS analysis, adjust the sample extract volume to approximately 500 μL. This is done by adding 50 μL of the recovery standard spike solution (Section 7.2.5, and Table 4 or 4A) to the 450 μL final volume (Section 6.6.2) of the

concentrated sample extract give the sample extract concentration required by Table 8 or 8A. If the sample volume must be changed to achieve a desired detection limit, the recovery spike solution concentration must be adjusted accordingly to achieve the target concentrations of Table 8 or 8A.

Inject a 2 µL aliquot of the sample extract (Section 6.6.2) on to the DB-5 column. Use the same volume as that used during calibration. Recommended GC/MS operating conditions are described in Section 7.3.

The presence of a given PAH is qualitatively confirmed if the criteria of Section 7.6.1 are satisfied.

The response for any quantitation or confirmation ion in the sample extract must not exceed the response of the highest concentration calibration standard.

Collect, record, and store the data for the calculations required by Sections 9.1.7, 9.1.8, 9.1.9, and 9.1.10. Report the results as required by Section 10.2.

7.6 QUALITATIVE ANALYSIS

7.6.1 Identification Criteria

7.6.1.1 Ion Criteria

For LRMS analysis, all quantitation and confirmation ions (Table 13) must be present.

7.6.1.2 Relative Retention Time (RRT) Criteria

The relative retention time (RRT) of the analyte compared to the RRT for the ^{2}H-standards must be within ±0.008 RRT units of the relative retention times obtained from the continuing calibration (or initial calibration if this applies).

7.6.1.3 Signal to Noise Ratio

The signal to mean noise ratio must be 10:1 for the internal standards. This ratio for the unlabelled compounds must be greater than 2.5 to 1 for the quantitation ions for HRMS and for both quantitation and confirmation ions for LRMS.

If broad background interference restricts the sensitivity of the GC/MS analysis, the analyst must employ additional cleanup on the archive sample and reanalyze.

7.7 QUANTITATIVE ANALYSIS

7.7.1 Relative Response Factors (RRFs)

7.7.1.1 RRF for Unlabelled PAH and Surrogate Standards from Initial Calibration Data

Use the results of the calibration and Equation 429-13 to calculate the relative response factors (RRFs) for each calibration compound and surrogate standard in each calibration

solution (Tables 5 or 5A). Table 11 shows the assignments of the internal standards for calculation of the RRFs for the calibration solution shown in Table 5. Table 11A shows the assignments of the internal standards for calculation of the RRFs for the calibration solution shown in Table 5A. Report the results as required by Section 10.2.

7.7.1.2   RRF for Determining Internal Standard Recovery

Use the results of the calibration in Equation 429-18 to calculate the relative response factor for each internal standard relative to an appropriate recovery standard. Table 11 shows the assignments of the recovery standards for calculating internal standard recoveries for the calibration solution shown in Table 5. Table 11A shows the assignments of the recovery standards for calculating internal standard recoveries for the calibration solution shown in Table 5A. Report the results as required by Section 10.2.

7.7.1.3   RRF for Determining Alternate Standard Recovery

Use the calibration results and Equation 429-19 to calculate the response factor for the alternate standard relative to the appropriate recovery standard. Table 11 shows the assignment of the recovery standards for calculating alternate standard recovery for the calibration solution shown in Table 5. for the calibration solution shown in Table 5. Report the results as required by Section 10.2.

7.7.1.4   Mean Relative Response Factor

Use Equation 429-20 to calculate the mean RRF for each compound (unlabelled calibration standards, surrogate standards, internal standards and alternate standard). This is the average of the five RRFs calculated for each compound (one RRF calculated for each calibration solution). The mean RRF may be used if the linearity criterion of Section 7.7.2 is satisfied.

Report the results as required by Section 10.2.

7.7.1.5   RRF from Continuing Calibration Data

Analyze one or more calibration standards (one must be the medium level standard) on each work shift of 12 hours or less. Use Equations 429-17, 429-18, and 429-19 to calculate the RRFs for each analyte. Use Equation 429-22 to calculate ΔRRF, the relative percent difference between the daily RRF and the mean RRF calculated during initial calibration Check whether the performance criterion of Section 7.4.2B is satisfied. Report the results as required by Section 10.2.

7.7.2   Relative Standard Deviation of Relative Response Factors

For each analyte, calculate the sample standard deviation (SD) of the RRFs used to calculate the mean RRF. Use Equation 429-21 to calculate the percent relative standard deviation (%RSD) for each analyte. The analyst may use the mean RRF if the percent relative standard deviation of the RRFs is 30% or less. If the RSD requirement is not satisfied, analyze additional aliquots of appropriate calibration solutions to obtain an acceptable RSD of RRFs over the entire

concentration range, or take action to improve GC/MS performance. Otherwise, use the complete five point calibration curve for that compound.

8 QUALITY ASSURANCE/QUALITY CONTROL

Each laboratory that uses this method is required to operate a formal quality control program. The minimum quality control requirements of this program consists of an initial demonstration of laboratory capability (according to Sections 7.3 and 8.1.3.1), and periodic analysis of blanks and spiked samples as required in Sections 8.1.1 and 8.1.3.2 as a continuing check on performance.

The laboratory must maintain performance records to document the quality of data that are generated. The results of the data quality checks must be compared with the method performance criteria to determine if the analytical results meet the performance requirements of the method. The laboratory must generate accuracy statements as described in Section 8.4.1.

8.1   QA SAMPLES

8.1.1   Laboratory Method Blank

The analyst must run a laboratory method blank with each set of 15 or fewer samples. The method blank must be a resin sample from the same batch used to prepare the sampling cartridge and the laboratory control samples. The method blank must be prepared and stored as described in Sections 4.3.4 and 4.3.5.

The analyst shall perform all of the same procedures on the method blank as are performed on the solid samples (Section 6.5.2.1) from the beginning of sample extraction through to the end of the GC/MS analytical procedures.

8.1.2   Performance Evaluation Samples

The laboratory should analyze performance evaluation samples quarterly when these samples become available. These samples must be prepared and analyzed by the same methods used for the field samples. Performance for the most recent quarter should be reported with the results of the sample analysis.

8.1.3   Laboratory Control Sample (LCS)

8.1.3.1   Initial Demonstration of Laboratory Capability

Before performing sample analyses for the first time, the analyst shall demonstrate the ability to generate results of acceptable precision and accuracy by using the following procedures.

Prepare spiking solutions from stock standards prepared independently from those used for calibration. Spike at least four resin samples cleaned as described in Section 4.2.2 with each of the target unlabelled analytes as indicated in Table 9. Blank resin contamination levels must be no greater than 10 percent of the levels of the spiked analytes. Add the amounts of

internal standards required by Table 7 or 7A. Add the alternate standard to the extract to monitor the efficiency of the cleanup procedure.

The LCS spikes shall undergo all of the same procedures as are performed on the solid samples (Section 6.5.1.2) from the beginning of sample extraction through to the end of the GC/MS analytical procedures.

Calculate:

(A)　percent recoveries for the internal standards and alternate standard,
(B)　the mass of each target analyte in μg/sample or ng/sample,
(C)　the average of the results for the four analyses in μg/sample or ng/sample,
(D)　the average recovery (R) as a percentage of the amount added, and
(E)　the relative standard deviation S_R.

Report the results as required by Section 10.2.4.

If all the acceptance criteria of Section 8.2.6 are satisfied for all of the target PAH, the analyst may begin analysis of blanks and samples. Otherwise, corrective action must be taken as required by Section 8.2.6.

8.1.3.2　　Ongoing Analysis of LCS

The analyst must run two laboratory control samples with each set of 15 or fewer samples. The resin for the LCS must be taken from the same batch used to prepare the sampling cartridge and the laboratory method blank. The LCS resin must be prepared and stored as described in Sections 4.3.4 and 4.3.5.

Prepare spiking solutions from stock standards prepared independently from those used for calibration. Spike each resin sample with each of the target unlabelled analytes as indicated in Table 9. Blank resin contamination levels must be no greater than 10 percent of the levels of the spiked analytes. Add the amounts of internal standards required by Table 7 or 7A. Add the alternate standard to the extract to monitor the efficiency of the cleanup procedure

The LCS spikes shall undergo all of the same procedures as are performed on the solid samples (Section 6.5.1.2) from the beginning of sample extraction through to the end of the GC/MS analytical procedures.

Calculate:

(A)　percent recoveries for the internal standards and alternate standard,
(B)　the mass of each target analyte in μg/sample or ng/sample,
(C)　the average of the results for the two analyses in μg/sample or ng/sample,
(D)　the average recovery as a percentage of the amount added, and
(E)　the relative percent difference for the two analyses.

Report the results as required by Section 10.2.

Add the results which satisfy the performance requirements of Section 8.2.6 to the results of the initial LCS analyses (8.1.3.1) and previous ongoing data for each compound in the LCS sample.

Update the charts as described in Section 8.4.1.

8.2   ACCEPTANCE CRITERIA

8.2.1   Blank Trains

The levels of any unlabelled analyte quantified in the blank train must not exceed 20 percent of the level of that analyte in the sampling train. If this criterion cannot be met, calculate a reporting limit that is five times the blank value (Equations 429-32 and 429-33). Do not subtract the blank value from the sample value.

8.2.2   Surrogate Standard Recovery

Acceptable surrogate (field spike) recoveries should range from 50 to 150 percent. If field spike recoveries are not within the acceptable range, this must be clearly indicated in the laboratory report. The affected sampling run must be identified in the report of the calculated emissions data.

8.2.3   Internal Standard Recovery

Recoveries for each of the internal standards must be greater than 50 percent and less than 150 percent of the known value.

If internal standard recoveries are outside of the acceptable limits, the signal to noise ratio of the internal standard must be greater than 10. Otherwise the analytical procedure must be repeated on the stored portion of the extract.

NOTE: This criterion is used to assess method performance. As this is an isotope dilution technique, it is, when properly applied, independent of internal standard recovery. Lower recoveries do not necessarily invalidate the analytical results for PAH, but they may result in higher detection limits than are desired.

If low internal standard recoveries result in detection limits that are unacceptable, the cleanup and GC/MS analysis must be repeated with the stored portion of the extract. If the analysis of the archive sample gives low recoveries and high detection limits, the results of both analyses must be reported.

8.2.4   Laboratory Method Blank

The laboratory method blank must not contain any of the target analytes listed in Table 1 at levels exceeding the PQL or 5 percent of the analyte concentration in the field sample.

If the method blank is contaminated, check solvents, reagents, standard solutions apparatus and glassware to locate and eliminate the source of contamination before any more samples are

analyzed. Table 3 shows those compounds that commonly occur as contaminants in the method blank, and the ranges of concentrations that have been reported.

If field samples were processed with a laboratory method blank that showed PAH levels greater than 5 percent of the field sample, they must be re-analyzed using the archived portion of the sample extract.

Recoveries of the internal standards must satisfy the requirements of 8.2.3. If the internal standard recoveries are less than 50%, the S/N ratio must be greater than 10 for the internal standard.

8.2.5   Performance Evaluation Sample

The following will be a requirement when performance evaluation samples become available, and performance criteria have been established:

Performance for the most recent quarter must be reported with the results of the sample analysis. If the performance criteria (to be established) are not achieved, corrective action must be taken and acceptable performance demonstrated before sample analysis can be resumed.

8.2.6   Laboratory Control Samples

8.2.6.1   Initial and Ongoing Analysis

The signal of each analyte in the initial and ongoing laboratory control samples must be at least 10 times that of the background.

Acceptable accuracy is a percent recovery between 50 and 150 percent. Acceptable precision for the initial LCS samples is a relative standard deviation (RSD) of 30 percent or less.

Acceptable precision for the ongoing analysis of duplicate samples is a relative percent difference of 50 percent or less.

If the RSD for the initial demonstration exceeds the precision limit, or any calculated recovery falls outside the range for accuracy, the laboratory performance for that analyte is unacceptable.

If the RPD for any ongoing duplicate analyses exceeds the precision limit, or any calculated recovery falls outside the range for accuracy, the laboratory performance for that analyte is unacceptable.

Beginning with Section 8.1.3.1, repeat the test for those analytes that failed to meet the performance criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.1.3.1 for the initial analysis and Section 8.3.1.2 for the ongoing analysis.

8.3 ESTIMATION OF THE METHOD DETECTION LIMIT (MDL) AND PRACTICAL QUANTITATION LIMIT (PQL)

8.3.1 Initial Estimate of MDL and PQL

The analyst shall prepare a batch of XAD-2 resin as described in Sections 4.2.2.1 to 4.2.2.3, then check for contamination as required by Section 4.2.2.4. Identify those PAH analytes present at background levels that are too high for the MDL determination. Use the procedure of Appendix A to calculate MDLs for the remaining target PAH compounds. The analyst may use any of the five approaches described in Appendix A (A1.1) to estimate an initial spike level for the MDL determination. One of the suggested approaches is based on a theoretical method quantitation limit (TMQL) estimated according to Equation 429-16.

$$ TMQL = C \ x \ \frac{V}{P} \ x \ 100 \ x \ 2 \qquad\qquad 429\text{-}16 $$

Where:

C = the concentration of the PAH in the lowest concentration calibration standard used in the initial calibration, (ng/μL)

V = the final extract volume, (μL)

P = the assumed percent recovery (50%) of the internal standard

2 = a factor to account for the fact that the final extract volume (V) contains one half of the analyte in the sample. The other half is archived.

8.3.2 Ongoing Estimation of MDL and PQL

Once every quarter in which this method is used, the analytical laboratory must analyze one spiked resin sample as described in Appendix A. Include all initial and quarterly results in the calculation of the standard deviation and MDL for each analyte that has not been identified as a common contaminant of the XAD-2 resin.

If the MDL for any analyte exceeds the MDL established during the initial determination, take corrective action as necessary, and repeat the monthly analysis. If any MDL still exceeds the initial MDL, then the initial standard deviation estimation procedure (Appendix A) must be repeated.

8.4 LABORATORY PERFORMANCE

The analyst must have documented standard operating procedures (SOPs) that contain specific stepwise instructions for carrying out this method. The SOPs must be readily available and followed by all personnel conducting the work. The SOP must be made available for review upon request by

the Executive Officer, the tester or reviewer of the analytical results. The analyst may impose restrictions on the dissemination of the information in the SOP.

The analyst must have documented precision and accuracy statements (Section 8.4.1) readily available.

The analyst must have results of the initial and ongoing estimates of the MDL (Sections 8.3.1 and 8.3.2) readily available.

8.4.1 Precision and Accuracy Statement

The precision and accuracy statements for the analytical procedure shall be based on the results of the initial and ongoing LCS analyses. The frequency of analysis is stated in Section 8.1.3.

Prepare a table of the recoveries and the relative percent difference for each ongoing analysis of the LCS and LCS duplicate. Figure 15A is an example of such a table. This must be included in the analytical data package submitted for each set of sample analyses.

Prepare a quality control chart for each target analyte that provides a graphic representation of continued laboratory performance for that target analyte. Figure 15B is an example QC chart for benzo(a)pyrene.

9 CALCULATIONS

Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation.

9.1 ANALYST'S CALCULATIONS

The analyst shall carry out the calculations described in Sections 9.1.1 to 9.1.11.

9.1.1 Relative Response Factors (RRF) for Unlabelled PAH and Surrogate Standards

Calculate the RRF for each target unlabelled PAH analyte and surrogate standard in each calibration solution . Use Equation 429-17 and the data obtained during initial calibration (7.3.7) or continuing calibration (7.4.1).

$$ RRF_s \; = \; \frac{A_s \; x \; Q_{is}}{A_{is} \; x \; Q_s} \qquad\qquad 429\text{-}17 $$

Where:

A_s = Area of the response for characteristic ions of the unlabelled analyte or surrogate standard (Tables 11 or 11A, 13, and 14).

A_{is} = Area of the response for characteristic ions of the appropriate internal standard (Tables 11 or 11A, 13, and 14).

Q_s = Amount of the unlabelled PAH calibration analyte or surrogate standard injected on to GC column, ng.

Q_{is} = Amount of the appropriate internal standard injected on to GC column, ng.

9.1.2 RRF for Determination of Internal Standard Recovery

Calculate RRF_{is} according to Equation 429-18, using data obtained from the analysis of the calibration standards.

$$RRF_{is} = \frac{A_{is} \times Q_{rs}}{A_{rs} \times Q_{is}} \qquad 429\text{-}18$$

Where:

A_{rs} = Area of the response for characteristic ions of the appropriate recovery standard (Tables 11 or 11A, 13, and 14).

Q_{rs} = Amount of the appropriate recovery standard injected on to GC column, ng.

9.1.3 RRF for Determination of Alternate Standard Recovery

Calculate RRF_{as} according to Equation 429-19, using data obtained from the analysis of the calibration standards.

$$RRF_{as} = \frac{A_{as} \times Q_{rs}}{A_{rs} \times Q_{as}} \qquad 429\text{-}19$$

Where:

A_{as} = Area of the response for characteristic ions of the alternate standard (Tables 13 and 14).

Q_{as} = Amount of alternate standard injected on to the GC column, ng.

9.1.4 Mean Relative Response Factors ($\overline{RRF}$)

Calculate the mean RRF for each target unlabelled PAH, surrogate standard, internal standard and alternate standard using Equation 429-20 and the RRFs calculated according to Sections 9.1.1, 9.1.2, and 9.1.3.

$$\overline{RRF} = \frac{1}{n} \sum_{i=1}^{n} (RRF)_i \qquad 429\text{-}20$$

Where:

RRF$_i$ = RRF calculated for calibration solution "i" using one of Equations 429-17, 429-18 or 429-19.

n = The number of data points derived from the calibration. The minimum requirement is a five-point calibration (Section 7.2.3, Tables 5 and 6 or 6A)

9.1.5   Percent Relative Standard Deviation (%RSD) of Relative Response Factors

Use Equation 429-21 to calculate the relative standard deviation of the Relative Response Factors for each analyte.

$$\%RSD = \frac{SD}{\overline{RRF}} \times 100\%$$ 429-21

Where:

$\overline{RRF}$ = Mean relative response factor of a given analyte as defined in Sections 7.7.1.4 and 9.1.4.

SD = The sample standard deviation of the relative response factors used to calculate the mean RRF.

9.1.6   Continuing Calibration ΔRRF

Use Equation 429-22 to calculate ΔRRF, the relative percent difference (RPD) between the daily RRF and the mean RRF calculated during initial calibration.

$$\Delta RRF = \frac{RRF_c - \overline{RRF}}{\overline{RRF}} \times 100\%$$ 429-22

Where: —

RRF$_c$ = The RRF of a given analyte obtained from the continuing calibration (Section 7.4).

9.1.7   Percent Recovery of Internal Standard, R_{is}

Calculate the percent recovery, R_{is} for each internal standard in the sample extract, using Equation 429-23.

$$R_{is} = \frac{A_{is}' \times Q_{rs}}{A_{rs} \times \overline{RRF_{is}} \times Q_{is}} \times 100\% \qquad \text{429-23}$$

Where:

$\overline{RRF}_{is}$ = Mean relative response factor for internal standard (Equations 429-18 and 429-20).

9.1.8   Percent Recovery of Surrogate Standard, R_{ss}

Calculate the percent recovery, R_{ss} for each surrogate standard in the sample extract, using Equation 429-24.

$$R_{ss} = \frac{A_{ss} \times Q_{is}}{A_{is} \times \overline{RRF_s} \times Q_{ss}} \times 100\% \qquad \text{429-24}$$

Where:

A_{ss} = Area of the response for characteristic ions of the surrogate standard (Tables 13 and 14).

Q_{ss} = Amount of the surrogate standard added to resin cartridge before sampling, ng.

$\overline{RRF}_s$ = Mean relative response factor for surrogate standard (Equations 429-17 and 429-20).

9.1.9   Percent Recovery of Alternate Standard, R_{as}

Calculate the percent recovery, R_{as} for the alternate standard in the sample extract, using Equation 429-25.

$$R_{as} = \frac{A_{as} \times Q_{rs}}{A_{rs} \times \overline{RRF_{as}} \times Q_{as}} \times 100\% \qquad \text{429-25}$$

Where:

$$\overline{RRF}_{as} = \text{Mean relative response factor for alternate standard (Equations 429-19 and 429-20).}$$

9.1.10   Mass of the Target Analytes and Surrogate Standards in
Emissions Sample or Blank Train

Use Equation 429-26 to determine the total mass of each PAH compound or surrogate standard in the sample:

Report the PQL (9.1.11) for those analytes that were not present at levels higher than the PQL provided to the tester prior to testing (2.3.3).

$$M = \frac{Q_{is} \times A_s}{A_{is} \times \overline{RRF}} \qquad\qquad 429\text{-}26$$

Where:

M $=$ Mass (ng) of surrogate standard (M_s) or target analyte (M_t) detected in the sample.

Q_{is} $=$ Amount of internal standard or surrogate standard added to each sample.

A_s $=$ Area of the response for characteristic ions of the unlabelled analyte or surrogate standard (Tables 13 and 14).

A_{is} $=$ Area of the response for characteristic ions of the appropriate internal standard (Tables 13, and 14).

$\overline{RRF}$ $=$ Mean relative response factor of a given analyte calculated as required by Sections 7.7.1.4 and 9.1.4.

9.1.11   Analytical Reporting Limit

The analyst shall report the PQL (Section 2.3.3) for those analytes that were not present in the emissions sample or blank train at levels higher than the pre-test estimate of the PQL.

9.2   TESTER'S CALCULATIONS

9.2.1   Sample/Blank Train PAH Mass Ratio

Use Equation 429-27 to calculate the sample/blank train mass ratio for each PAH detected at levels above the MDL in both the field sample and the blank train.

$$RATIO = \frac{M_t}{M_{BT}} \qquad\qquad 429\text{-}27$$

Where:

M_t = Mass of target PAH analyte detected in the sampling train (Equation 429-26).

M_{BT} = Mass of the same PAH analyte detected in the blank train.

If the sample to blank train PAH mass ratio is less than five, calculate the reporting limit for the tested source as required by Section 9.2.4.2. Do not calculate M_c (Section 9.2.2) or M_e (Section 9.2.3) for the emissions report.

9.2.2 PAH Concentration in Emissions

Use Equation 429-28 to calculate the concentration in the emissions of 1) the PAH analytes detected in the sampling train but not in the blank train, and 2) the PAH analytes that satisfy the minimum sample to blank train mass ratio required by Section 9.2.1.

$$M_c = \frac{M_t}{V_{m(std)}} \quad x \quad \frac{1}{0.028317} \qquad \text{429-28}$$

Where:

M_c = Concentration of PAH in the gas, ng/dscm, corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29.92 in. Hg) on dry basis.

M_t = Mass of PAH compound in gas sample, ng (Equation 429-26)

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscf (Equation 429-10)

0.028317 = Factor for converting dscf to dscm.

9.2.3 PAH Mass Emission Rate

Use Equation 429-29 to calculate the mass emission rate for each PAH compound that satisfies the minimum sample/blank train PAH mass ratio (Section 9.2.1).

$$M_e = \frac{M_s}{V_{m(std)}} \quad x \quad \frac{Q_{std}}{60} \qquad \text{429-30}$$

Where:

M_e = Mass emission rate for PAH analyte, ng/second

M_t = Mass of PAH compound in the gas sample, ng (Equation 429-26)

Q_{std} =   Average stack gas dry volumetric flow rate corrected to standard conditions, dscf/min.

60   =   Factor for converting minutes to seconds

9.2.4   Source Reporting Limit

9.2.4.1   PAH Not Detected in Either Sampling or Blank Train

Use Equation 429-30 or 429-31 to calculate the reporting limit for those analytes that were not detected at levels above the PQL in either the sampling or blank train.

$$RL_{cs} = \frac{PQL}{V_{m(std)}} \times \frac{1}{0.028317} \qquad \text{429-30}$$

$$RL_{es} = \frac{PQL}{V_{m(std)}} \times \frac{Q_{std}}{60} \qquad \text{429-31}$$

Where:

Rl_{cs} =   Reporting limit for the tested source, (ng/dscm), corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29-92 in. Hg) on dry basis.

Rl_{es} =   Reporting limit for the tested source, (ng/sec.).

0.028317   =   Factor for converting dscf to dscm.

60   =   Factor for converting minutes to seconds.

9.2.4.2   PAH Detected in Blank Train and Sample/Blank Train Ratio <5

If the sample to blank train PAH mass ratio is less than five, then Equation 429-32 or 429-33 shall be used to calculate the reporting limit for that PAH.

$$RL_{cb} = \frac{5 \times M_{BT}}{V_{m(std)}} \times \frac{1}{0.028317} \qquad \text{429-32}$$

$$RL_{eb} = \frac{5 \times M_{BT}}{V_{m(std)}} \times \frac{Q_{std}}{60} \qquad \text{429-33}$$

Where:

RI_{cb} =   Reporting limit for the tested source, (ng/dscm), corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29-92 in. Hg) on dry basis.

RI_{cb} =   Reporting limit for the tested source, (ng/sec.).

M_{BT} =   The total mass of that PAH analyte in the field blank train.

10 REPORTING REQUIREMENTS

The source test protocol must contain all the sampling and analytical data required by Sections 2.2 to 2.5, 4.2.1.1, and 4.2.2.4, as well as the information listed in Sections 10.1 and 10.2 that pertain to identification and quantitation of the samples.

The emissions test report must contain all of the sampling and analytical data necessary to calculate emissions values for the target analytes or to demonstrate satisfactory performance of the method.

The end user or reviewer should be able to obtain from the source test report all information necessary to recalculate all reported test method results or to verify that all required procedures were performed.

Any deviations from the procedures described in this method must be documented in the analytical and sampling report.

10.1 SOURCE TEST PROTOCOL

At a minimum, the source test protocol must include all of the data required by Section 2.2 and the information listed in Sections 10.1.1 through 10.1.4.

10.1.1 Preparation of Filters

A. Manufacturer's lot number for the batch of filters to be used in the test.

B. Contamination check of filter (Section 4.2.1.1)

     (i)   Date of cleaning.
     (ii)   Date of PAH analysis.
     (iii)   Table of results of PAH analysis required by Section 4.2.1. The analytical report must include all of the data listed in Section 10.2.

C. Storage conditions prior to the test (4.3.3)

10.1.2 Preparation of XAD-2 resin

A. ID for the batch to be used in the test. The same batch must be used for the sampling train and the laboratory QC samples.

B. Contamination check of resin (Sections 4.2.2.1 to 4.2.2.4)

     (i)   Date of cleaning.
     (ii)   Date of PAH analysis.

(iii) Table of results of PAH analysis required by Section 4.2.2.4. The analytical report must include all of the data listed in Section 10.2.

C. Addition of surrogate standards to the resin cartridge.

(i) Amount of each compound.
(ii) Date of spiking.

D. Storage conditions prior to the test (Section 4.3.3)

10.1.3 Method Detection Limits and Practical Quantitation Limits

The MDL and PQL for each target analyte determined as required by Sections 2.3.2 and 2.3.3.

10.1.4 Target Sampling Parameters

A. Source target concentration of each emitted PAH of interest.

B. Results of calculations required by Sections 2.5.2 to 2.5.5.

Figure 9 shows the minimum required calculations of target sampling parameters.

10.2 LABORATORY REPORT

The analyst must generate a laboratory report for each pre-test analysis of the sampling media (Sections 2.3, 4.2.2.1, and 4.2.2.4) and each post-test analysis of the sampling trains and laboratory QC samples.

A minimum of 7 post-test analyses are required to determine the emissions from the source and to document the quality of the emissions data. These are the analyses of three sampling runs, one blank train, one laboratory method blank and two laboratory control samples.

At a minimum, any report (data package) from the analyst to the tester shall contain the information listed in Sections 10.2.1 to 10.2.6 pertaining to identification and PAH quantitation of all samples.

10.2.1 Five-point Initial Calibration

The report of the results of the initial five-point calibration must include the data listed in A, B, and C below:

A. Mass chromatograms for each initial calibration solution that show at a minimum:

(i) Instrument ID,
(ii) laboratory sample ID on each chromatogram.
(iii) date and time of GC/MS analysis,
(iv) mass of monitored ions for each compound in the calibration solution - unlabelled PAH, internal standard, surrogate standard, alternate standard and recovery standard,
(v) retention time for each compound in the calibration solution, and

(vi) · either peak height or area of the signals observed for the monitored ion masses.

B. A summary table of the data obtained for each initial calibration solution that shows at a minimum:

    (i)   Instrument ID,
    (ii)   laboratory sample ID,
    (iii)   date and time of GC/MS analysis,
    (iv)   retention time for each compound - unlabelled PAH, internal standard, surrogate standard, alternate standard and recovery standard,
    (v)   relative retention time for each unlabelled PAH,
    (vi)   either peak height or area of the signals observed for the monitored ion masses,
    (vii)   the relative response factors for each unlabelled PAH, internal standard, surrogate standard, and alternate standard, and
    (viii) analyst's signature

Figure 14A is an example of a summary table that contains the minimum required information for the analysis of a single calibration solution.

C. A summary table that shows at a minimum:

    (i)   Instrument ID,
    (ii)   the date and time of the GC/MS analysis,
    (iii)   the relative response factor (RRF) calculated for each unlabelled PAH, internal standard, surrogate standard, and alternate standard in each calibration solution,
    (iv)   the average relative response factor ($\overline{RRF}$) calculated for the five point calibration,
    (v)   the relative standard deviation of the relative response factors, and
    (vi)   the recovery of each internal standard in percent.

Figure 14B is an example of a report that contains the minimum required information for a five point calibration summary.

10.2.2   Continuing Calibration

The report of the results of a continuing calibration must include the data listed in 10.2.2 A, B, and C below:

A. Mass chromatogram that shows at a minimum the information listed in 10.2.1 A.

B. A summary table of the raw data obtained for the continuing calibration that shows at a minimum, the information listed in 10.2.1 B.

C. A summary table that shows at a minimum:

    (i)   the relative response factor (RRF) for each unlabelled PAH, internal standard, surrogate standard, and alternate standard in the continuing calibration solution,
    (ii)   the average relative response factor ($\overline{RRF}$) for each compound calculated for the five point calibration,

(iii) ΔRRF for each unlabelled PAH, internal standard, surrogate standard, and alternate standard in the continuing calibration solution,

(iv) the recovery of each internal standard in percent.

Figure 14C is an example of a summary report that contains the minimum information required by Section 10.2.2C for the analysis of the continuing calibration solution.

10.2.3   Laboratory Method Blank

The laboratory report of the results of the analysis of the method blank must include at a minimum the data listed in 10.2.3 A, B, and C below:

A. Mass chromatograms that show at a minimum the information listed in 10.2.1 A.

B. A summary table of the data obtained for each method blank that shows at a minimum, the information listed in 10.2.5 B.

C. A summary table that reports the same data as listed in 10.2.5 C below.

10.2.4   Laboratory Control Samples

The report of the results of the analysis of the LCS samples must include at a minimum the data listed in 10.2.4 A, B, and C below:

A. Mass chromatograms that show at a minimum the information listed in 10.2.1 A.

B. A summary table of the raw data for each sample that shows at a minimum, the information listed in 10.2.1 B, and in addition:

(i)   Client's sample ID
(ii)   mass of each analyte,
(iii) the recovery of each internal standard, and alternate standard,

Figure 16A is an example of a summary table that contains the minimum information required by 10.2.4 B.

C. A summary table that reports for the two LCS analyses:

(i)   client's sample ID,
(ii)   sample matrix description,
(iii) date of cleaning of the XAD-2 resin,
(iv)   lot number for the resin (resin for all field samples and QA samples must come from the same lot),
(v)   date of extraction of LCS samples,

Figure 15A is an example of a summary table that contains the minimum information required by 10.2.4 C.

10.2.5   Emissions Samples

The report of the results of the analyses of the three sampling trains and the blank train must
include the data listed in 10.2.5 A, B, and C below:

A. Mass chromatograms that show at a minimum the information listed in 10.2.1 A, and in
    addition,

    (i)   client's sample ID

B. A summary table of the data for the analysis of each sample that shows at a minimum, the
    information listed in 10.2.1 B, and in addition,

    (i)   client's sample ID
    (ii)   Date of five point initial calibration (ICAL)
    (iii) ICAL ID,
    (iv)   mass of each analyte,
    (v)   the recovery of each internal standard, alternate standard and surrogate standards in
           percent

Figure 16A is an example of a summary table that contains the minimum information required
by 10.2.5 B.

C. A summary table that reports:

    (i)   client's sample ID (from a chain of custody record submitted by the tester),
    (ii)   sample matrix description,
    (iii) date of cleaning of the XAD-2 resin,
    (iv)   lot number for the resin (resin for all field samples and QA samples must come from
           the same lot),
    (v)   date of submittal of the tester's samples
    (vi)   date of extraction of samples,
    (vii) Initial calibration Run ID,
    (viii) Continuing calibration ID

Figure 16B is an example of a summary table that contains the minimum information required
by 10.2.5C.

10.2.6   Data Flags

The laboratory report must include an explanation of any qualifiers that are used to indicate
specific qualities of the data.

10.3   EMISSIONS TEST REPORT

The emissions test report should include narrative that describes how the test was done. The tester's
report must also include all the appropriate sections used in a report from a Method 5 test such as a
description of the plant process, sampling port locations, control equipment, fuel being used, general

plant load conditions during the test (description of plant production equipment problems, etc.), and anything else necessary to characterize the condition being tested.

The tester's report must also include all of the information listed in Sections 10.3.1 to 10.3.4.

10.3.1   Tester's Summary of Analytical Results

The tester must summarize the results of the minimum seven analyses required for each source test. At a minimum, the summary must contain the information listed in Figure 17A including all data flags.

The tester must obtain the detailed analytical results (Section 10.2) from the laboratory and include them in the appendices as required below.

10.3.2   Field Data Summary

The report from the tester to the end user must contain a field data summary. This summary must include at a minimum a table of the results of the calculations required by Section 4.5. as well as the values which were used to calculate the reported results. Figure 17B is an example of a field data summary that contains the minimum required information.

10.3.3   PAH Emissions Results

Figure 17C show the calculations of the concentrations and mass emission rates of the target PAH. The reviewer should be able to use the data in Figures 17A and 17B to check the calculations in Figure 17C. The reviewer should also be able to check the appendix to the report to determine the accuracy and the quality of the data summarized by the tester in Figures 17A and 17B.

10.3.4   Appendix to the Emissions Test Report

At a minimum, the following raw data or signed copies must be included in an appendix to the emissions test report.

A. Record of data for sample site selection and minimum number of traverse points.

B. Moisture determination for isokinetic settings.

C. Velocity traverse data.

D. Gas analysis for determination of molecular weight.

E. Calibration records.

F. Method 429 sampling run sheets.

G. PAH laboratory reports listed in Section 10.2

The information listed above is to be considered as the minimum that should be included to characterize a given operating condition. The end user or the executive officer may require additional information for any given project.

11 BIBLIOGRAPHY

11.1   U.S. Environmental Protection Agency/Office of Water Engineering and Analysis Division (4303), Washington D.C., Method 1613. Tetra-through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS. EPA 821-B-94-005. (1994).

11.2   U.S. Environmental Protection Agency/Office of Solid Waste, Washington D.C., Method 3611A. Alumina Column Cleanup and Separation of Petroleum Wastes. In "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods" SW-846 (1986).

11.3   U.S. Environmental Protection Agency/Office of Solid Waste, Washington D.C., Method 3630B. Silica Gel Cleanup. In "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods" SW-846 (1986).

11.4   Thomason, J.R., ed., Cleaning of Laboratory Glassware. Section 3, A, pp 1-7 in "Analysis of Pesticide Residues in Human and Environmental Samples", Environmental Protection Agency, Research Triangle Park, N.C. (1974).

11.5   ARB Method 428. Determination of Polychlorinated Dibenzo-p-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Emissions From Stationary Sources. September, 1990.

11.6   U. S. Environmental Protection Agency, Method 1625 Revision B - Semivolatile Organic Compounds by Isotope Dilution. 40 CFR Ch.1 (7-1-95 Edition) Pt. 136, App. A.

11.7   Rom, Jerome J., Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. Environmental Protection Agency. Research Triangle Park, NC. APTD-0576. March, 1972.

11.8   Shigehara, R.T., Adjustments in the EPA Nomograph for Different Pitot Tube Coefficients and Dry Molecular Weights. Stack Sampling News, 2: 4-11. October, 1974

11.9   "Prudent Practices in the Laboratory. Handling and Disposal of Chemicals," National Academy Press. Washington D.C. 1995.

TABLE 1

METHOD 429 TARGET ANALYTES

Naphthalene

2-Methylnaphthalene

Acenaphthene

Acenaphthylene

Fluorene

Phenanthrene

Anthracene

Fluoranthene

Pyrene

Benzo(a)anthracene

Chrysene

Benzo(b)fluoranthene

Benzo(k)fluoranthene

Benzo(e)pyrene

Benzo(a)pyrene

Perylene

Indeno(1,2,3-cd)pyrene

Dibenz(a,h)anthracene

Benzo(ghi)perylene

TABLE 2

PRACTICAL QUANTITATION LIMITS FOR TARGET PAHs

	LRMS (μg/sample)	HRMS (ng/sample)	
Naphthalene	244	480	370
2-Methylnaphthalene	1.25	66	19
Acenaphthene	0.210	5.0	5.0
Acenaphthylene	0.104	5.0	5.0
Fluorene	0.207	16.5	5.5
Phenanthrene	0.85	22	14
Anthracene	0.146	5.0	5.0
Fluoranthene	0.346	5.0	5.0
Pyrene	0.191	5.0	5.0
Benzo(a)anthracene	0.167	5.0	5.0
Chrysene	0.272	5.0	5.0
Benzo(b)fluoranthene	1.119	5.0	5.0
Benzo(k)fluoranthene	0.738	5.0	5.0
Benzo(e)pyrene	0.146	5.0	5.0
Benzo(a)pyrene	0.191	5.0	5.0
Perylene	0.143	5.0	5.0
Indeno(1,2,3-cd)pyrene	0.798	5.0	5.0
Dibenz(a,h)anthracene	0.465	5.0	5.0
Benzo(ghi)perylene	0.305	5.0	5.0

TABLE 3
PAH ANALYSIS BY HRMS OF DIFFERENT LOTS OF CLEANED RESIN

PAH ANALYTES	CONCENTRATION (ng/sample)												
	SAMPLE IDENTIFICATION												
	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11	A12	A13
Naphthalene	480	220	198	120	350	340	320	360	370	380	340	520	220
2-Methylnaphthalene	65	32	38	15.6	32	15.6	32	26	19	45	15	32	48
Acenaphthylene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Acenaphthene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5,0	< 5.0
Fluorene	16.5	9.8	13	< 5.0	5.7	5.4	7.4	5.8	5.5	10	5.5	6.8	5.0
Phenanthrene	22	16	32	<12.5*	14	14.8	16	12	14	24	13	<13.0*	14
Anthracene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Fluoranthene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Pyrene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Benzo(a)anthracene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Chrysene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Benzo(b)fluoranthene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Benzo(k)fluoranthene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Benzo(e)pyrene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Benzo(a)pyrene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Perylene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Indeno(1,2,3-cd)pyrene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Dibenzo(a,h)anthracene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Benzo(g,h,i)perylene	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0

* 5 x the concentration of the lowest calibration standard

N-250

TABLE 4

COMPOSITION OF THE SAMPLE SPIKING SOLUTIONS

Spiking Solutions	Analytes	Concentration ng/µl LRMS	pg/µl HRMS
1.	**Surrogate Standards**		
	d_{10}-Fluorene	1.0	250
	d_{14}-Terphenyl	1.0	250
2.	**Internal Standards**		
	d_8-Naphthalene	1.0	100
	d_{10}-2-Methylnaphthalene	1.0	100
	d_8-Acenaphthylene	1.0	100
	d_{10}-Phenanthrene	1.0	100
	d_{10}-Fluoranthene	1.0	100
	d_{12}-Benzo(a)anthracene	1.0	100
	d_{12}-Chrysene	1.0	100
	d_{12}-Benzo(b)fluoranthene	1.0	200
	d_{12}-Benzo(k)fluoranthene	1.0	200
	d_{12}-Benzo(a)pyrene	1.0	200
	d_{12}-Perylene	1.0	200
	d_{12}-Indeno(1,2,3,c-d)pyrene	1.0	200
	d_{14}-Dibenz(a,h)anthracene	1.0	200
	d_{12}-Benzo(ghi)perylene	1.0	200
3.	**Alternate Standard**		
	d_{10}-Anthracene	1.0	100
4.	**Recovery Standards**		
	d_{10}-Acenaphthene	20.0	2000
	d_{10}-Pyrene	20.0	2000
	d_{12}-benzo(e)pyrene	20.0	2000

TABLE 4A

COMPOSITION OF ALTERNATIVE SAMPLE SPIKING SOLUTIONS

Spiking Solutions	Analytes	Concentration pg/µl HRMS
1A.	**Surrogate Standards**	
	d_{12}-Benzo(e)pyrene	250
	d_{14}-Terphenyl	250
2A.	**Internal Standards**	
	d_8-Naphthalene	100
	d_8-Acenaphthylene	100
	d_{10}-Acenaphthene	100
	d_{10}-Fluorene	100
	d_{10}-Phenanthrene	100
	d_{10}-Fluoranthene	100
	d_{12}-Benzo(a)anthracene	100
	d_{12}-Chrysene	100
	d_{12}-Benzo(b)fluoranthene	200
	d_{12}-Benzo(k)fluoranthene	200
	d_{12}-Benzo(a)pyrene	200
	d_{12}-Indeno(1,2,3,c-d)pyrene	200
	d_{14}-Dibenz(a,h)anthracene	200
	d_{12}-Benzo(ghi)perylene	200
3A.	**Alternate Standard**	
	d_{10}-Anthracene	100
4A.	**Recovery Standards**	
	d_{10}-2-Methylnaphthalene	2000
	d_{10}-Pyrene	2000
	d_{12}-Perylene	2000

TABLE 5

CONCENTRATIONS OF PAHs IN WORKING GC/MS CALIBRATION STANDARD
SOLUTIONS FOR LOW RESOLUTION MASS SPECTROMETRY

	CONCENTRATIONS (μg/μL)				
	Solutions				
	1	2	3	4	5
Calibration Standards					
Naphthalene	0.25	0.5	1.0	2.5	5.0
2-Methylnaphthalene	0.25	0.5	1.0	2.5	5.0
Acenaphthene	0.25	0.5	1.0	2.5	5.0
Acenaphthylene	0.25	0.5	1.0	2.5	5.0
Fluorene	0.25	0.5	1.0	2.5	5.0
Phenanthrene	0.25	0.5	1.0	2.5	5.0
Anthracene	0.25	0.5	1.0	2.5	5.0
Fluoranthene	0.25	0.5	1.0	2.5	5.0
Pyrene	0.25	0.5	1.0	2.5	5.0
Benzo(a)anthracene	0.25	0.5	1.0	2.5	5.0
Chrysene	0.25	0.5	1.0	2.5	5.0
Benzo(b)fluoranthene	0.25	0.5	1.0	2.5	5.0
Benzo(k)fluoranthene	0.25	0.5	1.0	2.5	5.0
Benzo(e)pyrene	0.25	0.5	1.0	2.5	5.0
Benzo(a)pyrene	0.25	0.5	1.0	2.5	5.0
Perylene	0.25	0.5	1.0	2.5	5.0
Indeno(1,2,3-cd)pyrene	0.25	0.5	1.0	2.5	5.0
Dibenz(a,h)anthracene	0.25	0.5	1.0	2.5	5.0
Benzo(ghi)perylene	0.25	0.5	1.0	2.5	5.0
Internal Standards					
d_8-Naphthalene	1.0	1.0	1.0	1.0	1.0
d_{10}-2-Methylnaphthalene	1.0	1.0	1.0	1.0	1.0
d_8-Acenaphthylene	1.0	1.0	1.0	1.0	1.0
d_{10}-Phenanthrene	1.0	1.0	1.0	1.0	1.0
d_{10}-Fluoranthene	1.0	1.0	1.0	1.0	1.0
d_{12}-Benzo(a)anthracene	1.0	1.0	1.0	1.0	1.0
d_{12}-Chrysene	1.0	1.0	1.0	1.0	1.0
d_{12}-Benzo(b)fluoranthene	1.0	1.0	1.0	1.0	1.0
d_{12}-Benzo(k)fluoranthene	1.0	1.0	1.0	1.0	1.0
d_{12}-Benzo(a)pyrene	1.0	1.0	1.0	1.0	1.0
d_{12}-Perylene	1.0	1.0	1.0	1.0	1.0
d_{12}-Indeno(1,2,3,c-d)pyrene	1.0	1.0	1.0	1.0	1.0
d_{14}-Dibenz(a,h)anthracene	1.0	1.0	1.0	1.0	1.0
d_{12}-Benzo(ghi)perylene	1.0	1.0	1.0	1.0	1.0

TABLE 5 (CONT)

CONCENTRATIONS OF PAHs IN WORKING GC/MS CALIBRATION STANDARD SOLUTIONS FOR LOW RESOLUTION MASS SPECTROMETRY

| | CONCENTRATIONS (ng/uL) | | | | |
| | Solutions | | | | |
	1	2	3	4	5
Surrogate Standards					
d_{10}-Fluorene	1.0	1.0	1.0	1.0	1.0
d_{14}-Terphenyl	1.0	1.0	1.0	1.0	1.0
Alternate Standard					
d_{10}-Anthracene	1.0	1.0	1.0	1.0	1.0
Recovery Standards					
d_{10}-Acenaphthene	1.0	1.0	1.0	1.0	1.0
d_{10}-Pyrene	1.0	1.0	1.0	1.0	1.0
d_{12}-benzo(e)pyrene	1.0	1.0	1.0	1.0	1.0

TABLE 6

CONCENTRATIONS OF PAHs IN WORKING GC/MS CALIBRATION STANDARD SOLUTIONS FOR HIGH RESOLUTION MASS SPECTROMETRY

	CONCENTRATIONS (µg/mL)				
	Solutions				
	1	2	3	4	5

Calibration Standards

	1	2	3	4	5
Naphthalene	10	50	100	200	500
2-Methylnaphthalene	10	50	100	200	500
Acenaphthylene	10	50	100	200	500
Acenaphthene	10	50	100	200	500
Fluorene	10	50	100	200	500
Phenanthrene	10	50	100	200	500
Anthracene	10	50	100	200	500
Fluoranthene	10	50	100	200	500
Pyrene	10	50	100	200	500
Benzo(a)anthracene	10	50	100	200	500
Chrysene	10	50	100	200	500
Benzo(b)fluoranthene	10	50	100	200	500
Benzo(k)fluoranthene	10	50	100	200	500
Benzo(e)pyrene	10	50	100	200	500
Benzo(a)pyrene	10	50	100	200	500
Perylene	10	50	100	200	500
Indeno(1,2,3-cd)pyrene	10	50	100	200	500
Dibenz(a,h)anthracene	10	50	100	200	500
Benzo(ghi)perylene	10	50	100	200	500

Internal Standards

	1	2	3	4	5
d_8-Naphthalene	100	100	100	100	100
d_8Methylnaphthalene	100	100	100	100	100
d_8-Acenaphthylene	100	100	100	100	100
d_{10}-Phenanthrene	100	100	100	100	100
d_{10}-Fluoranthene	100	100	100	100	100
d_{12}-Benzo(a)anthracene	100	100	100	100	100
d_{12}-Chrysene	100	100	100	100	100
d_{12}-Benzo(b)fluoranthene	200	200	200	200	200
d_{12}-Benzo(k)fluoranthene	200	200	200	200	200
d_{12}-Benzo(a)pyrene	200	200	200	200	200
d_{12}-Perylene	200	200	200	200	200
d_{12}-Indeno(1,2,3,c-d)pyrene	200	200	200	200	200
d_{14}-Dibenz(a,h)anthracene	200	200	200	200	200
d_{12}-Benzo(ghi)perylene	200	200	200	200	200

TABLE 6 (CONT)

CONCENTRATIONS OF PAHs IN WORKING GC/MS CALIBRATION STANDARD
SOLUTIONS FOR HIGH RESOLUTION MASS SPECTROMETRY

	CONCENTRATIONS (pg/uL)				
	Solutions				
	1	2	3	4	5
Surrogate Standards					
d_{10}-Fluorene	100	100	100	100	100
d_{14}-Terphenyl	100	100	100	100	100
Alternate Standard					
d_{10}-Anthracene	100	100	100	100	100
Recovery Standards					
d_{10}-Acenaphthene	200	200	200	200	200
d_{10}-Pyrene	200	200	200	200	200
d_{12}-benzo(e)pyrene	200	200	200	200	200

CONCENTRATIONS OF PAHs IN ALTERNATIVE WORKING GC/MS CALIBRATION
STANDARD SOLUTIONS FOR HIGH RESOLUTION MASS SPECTROMETRY

	CONCENTRATIONS (ng/μL)				
	Solutions				
	1	2	3	4	5

Calibration Standards

	1	2	3	4	5
Naphthalene	10	50	100	200	500
2-Methylnaphthalene	10	50	100	200	500
Acenaphthylene	10	50	100	200	500
Acenaphthene	10	50	100	200	500
Fluorene	10	50	100	200	500
Phenanthrene	10	50	100	200	500
Anthracene	10	50	100	200	500
Fluoranthene	10	50	100	200	500
Pyrene	10	50	100	200	500
Benzo(a)anthracene	10	50	100	200	500
Chrysene	10	50	100	200	500
Benzo(b)fluoranthene	10	50	100	200	500
Benzo(k)fluoranthene	10	50	100	200	500
Benzo(e)pyrene	10	50	100	200	500
Benzo(a)pyrene	10	50	100	200	500
Perylene	10	50	100	200	500
Indeno(1,2,3-cd)pyrene	10	50	100	200	500
Dibenz(a,h)anthracene	10	50	100	200	500
Benzo(ghi)perylene	10	50	100	200	500

Internal Standards

	1	2	3	4	5
d_8-Naphthalene	100	100	100	100	100
d_8-Acenaphthylene	100	100	100	100	100
d_{10}-Acenaphthene	100	100	100	100	100
d_{10}-Fluorene	100	100	100	100	100
d_{10}-Phenanthrene	100	100	100	100	100
d_{10}-Fluoranthene	100	100	100	100	100
d_{12}-Benzo(a)anthracene	100	100	100	100	100
d_{12}-Chrysene	100	100	100	100	100
d_{12}-Benzo(b)fluoranthene	200	200	200	200	200
d_{12}-Benzo(k)fluoranthene	200	200	200	200	200
d_{12}-Benzo(a)pyrene	200	200	200	200	200
d_{12}-Indeno(1,2,3,c-d)pyrene	200	200	200	200	200
d_{14}-Dibenz(a,h)anthracene	200	200	200	200	200
d_{12}-Benzo(ghi)perylene	200	200	200	200	200

CONCENTRATIONS OF PAHs IN ALTERNATIVE WORKING GC/MS CALIBRATION STANDARD SOLUTIONS FOR HIGH RESOLUTION MASS SPECTROMETRY

	CONCENTRATIONS (pg/uL)				
	Solutions				
	1	2	3	4	5
Surrogate Standards					
d_{12}-benzo(e)pyrene	100	100	100	100	100
d_{14}-Terphenyl	100	100	100	100	100
Alternate Standard					
d_{10}-Anthracene	100	100	100	100	100
Recovery Standards					
d_{10}-2-Methylnaphthalene	200	200	200	200	200
d_{10}-Pyrene	200	200	200	200	200
d_{12}-Perylene	200	200	200	200	200

TABLE 7

SPIKE LEVELS FOR LABELLED STANDARDS

Time of Addition	Analyte	LRMS (µg/sample)	HRMS (ng/sample)
Before sampling	**Surrogate Standards**		
	d_{10}-Fluorene	2.0	500
	d_{14}-Terphenyl	2.0	500
Before extraction	**Internal Standards**		
	d_8-Naphthalene	2.0	200
	d_{10}-2-Methylnaphthalene	2.0	200
	d_8-Acenaphthylene	2.0	200
	d_{10}-Phenanthrene	2.0	200
	d_{10}-Fluoranthene	2.0	200
	d_{12}-Benzo(a)anthracene	2.0	200
	d_{12}-Chrysene	2.0	200
	d_{12}-Benzo(b)fluoranthene	2.0	400
	d_{12}-Benzo(d)fluoranthene	2.0	400
	d_{12}-Benzo(a)pyrene	2.0	400
	d_{12}-Perylene	2.0	400
	d_{12}-Indeno(1,2,3,c-d)pyrene	2.0	400
	d_{14}-Dibenz(a,h)anthracene	2.0	400
	d_{12}-Benzo(ghi)perylene	2.0	400
Before extraction	**Alternate Standard**		
	d_{10}-Anthracene	2.0	200
Before GC/MS	**Recovery Standards**		
	d_{10}-Acenaphthene	1.0	100
	d_{10}-Pyrene	1.0	100
	d_{12}-benzo(e)pyrene	1.0	100

TABLE 7A

SPIKE LEVELS FOR LABELLED STANDARDS FOR ALTERNATIVE HRMS SPIKING SCHEME

Time of Addition	Analyte	HRMS (ng/sample)
Before sampling	**Surrogate Standards**	
	d_{12}-benzo(e)pyrene	500
	d_{14}-Terphenyl	500
Before extraction	**Internal Standards**	
	d_8-Naphthalene	200
	d_8-Acenaphthylene	200
	d_{10}-Acenaphthene	200
	d_{10}-Fluorene	200
	d_{10}-Phenanthrene	200
	d_{10}-Fluoranthene	200
	d_{12}-Benzo(a)anthracene	200
	d_{12}-Chrysene	200
	d_{12}-Benzo(b)fluoranthene	400
	d_{12}-Benzo(d)fluoranthene	400
	d_{12}-Benzo(a)pyrene	400
	d_{12}-Indeno(1,2,3,c-d)pyrene	400
	d_{14}-Dibenz(a,h)anthracene	400
	d_{12}-Benzo(ghi)perylene	400
Before extraction	**Alternate Standard**	
	d_{10}-Anthracene	200
Before GC/MS	**Recovery Standards**	
	d_{10}-2-Methylnaphthalene	100
	d_{10}-Pyrene	100
	d_{12}-Perylene	100

TABLE 8

TARGET CONCENTRATIONS FOR LABELLED STANDARDS IN SAMPLE EXTRACT[1]

	ng/μl LRMS	pg/μl HRMS
Surrogate Standards		
d_{10}-Fluorene	2.0	500
d_{14}-Terphenyl	2.0	500
Internal Standards		
d_8-Naphthalene	2.0	200
d_{10}-2-Methylnaphthalene	2.0	200
d_8-Acenaphthylene	2.0	200
d_{10}-Phenanthrene	2.0	200
d_{10}-Fluoranthene	2.0	200
d_{12}-Benzo(a)anthracene	2.0	200
d_{12}-Chrysene	2.0	200
d_{12}-Benzo(b)fluoranthene	2.0	400
d_{12}-Benzo(k)fluoranthene	2.0	400
d_{12}-Benzo(a)pyrene	2.0	400
d_{12}-Perylene	2.0	400
d_{12}-Indeno(1,2,3,c-d)pyrene	2.0	400
d_{14}-Dibenz(a,h)anthracene	2.0	400
d_{12}-Benzo(ghi)perylene	2.0	400
Alternate Standard		
d_{10}-Anthracene	1.0	200
Recovery Standards		
d_{10}-Acenaphthene	1.0	200
d_{10}-Pyrene	1.0	200
d_{12}-benzo(e)pyrene	1.0	200

[1] Assuming 100 percent recovery.

TABLE 8A

TARGET CONCENTRATIONS FOR LABELLED STANDARDS IN SAMPLE EXTRACT OBTAINED WITH ALTERNATIVE HRMS SPIKING SCHEME[1]

	pg/µl HRMS
Surrogate Standards	
d_{12}-benzo(e)pyrene	500
d_{14}-Terphenyl	500
Internal Standards	
d_8-Naphthalene	200
d_8-Acenaphthylene	200
d_{10}-Acenaphthene	200
d_{10}-Fluorene	200
d_{10}-Phenanthrene	200
d_{10}-Fluoranthene	200
d_{12}-Benzo(a)anthracene	200
d_{12}-Chrysene	200
d_{12}-Benzo(b)fluoranthene	400
d_{12}-Benzo(k)fluoranthene	400
d_{12}-Benzo(a)pyrene	400
d_{12}-Indeno(1,2,3,c-d)pyrene	400
d_{14}-Dibenz(a,h)anthracene	400
d_{12}-Benzo(ghi)perylene	400
Alternate Standard	
d_{10}-Anthracene	200
Recovery Standards	
d_{10}-2-Methylnaphthalene	200
d_{10}-Pyrene	200
d_{12}-Perylene	200

[1] Assuming 100 percent recovery.

TABLE 9

CONCENTRATIONS OF COMPOUNDS IN LABORATORY CONTROL SPIKE SAMPLE

	ng/sample	
	LRMS	HRMS
Unlabelled Compounds		
Naphthalene	2.0	1000
2-Methylnaphthalene	2.0	200
Acenaphthylene	2.0	200
Acenaphthene	2.0	200
Fluorene	2.0	200
Phenanthrene	2.0	500
Anthracene	2.0	200
Fluoranthene	2.0	200
Pyrene	2.0	200
Benzo(a)anthracene	2.0	200
Chrysene	2.0	200
Benzo(b)fluoranthene	2.0	200
Benzo(k)fluoranthene	2.0	200
Benzo(e)pyrene	2.0	200
Benzo(a)pyrene	2.0	200
Perylene	2.0	200
Indeno(1,2,3,c-d)pyrene	2.0	200
Dibenz(a,h)anthracene	2.0	200
Benzo(ghi)perylene	2.0	200
Alternate Standard		
d_{10}-Anthracene	2.0	200

TABLE 10

RECOMMENDED GAS CHROMATOGRAPHIC OPERATING CONDITIONS FOR PAH ANALYSIS

Column Type	DB-5
Length (m)	30
ID (mm)	0.25
Film Thickness (μm)	0.32
Helium Linear Velocity (cm/sec)	30
Injection mode	Splitless
Splitless Time (sec)	30
Initial Temperature (°C)	45
Initial Time (min)	4
Program Rate (°C/min)	8
Final Temperature (°C)	300
Final Hold Time	until benzo(ghi) perylene has eluted
Injector Temperature (°C)	320

TABLE 11

ASSIGNMENTS OF INTERNAL STANDARDS FOR CALCULATION CF RRFs AND QUANTITATION OF TARGET PAHs AND SURROGATE STANDARDS

Analyte	Internal Standards
Unlabeled PAH	
Naphthalene	d_8-Naphthalene
2-Methylnaphthalene	d_{10}-2-Methylnaphthalene
Acenaphthylene	d_8-Acenaphthylene
Acenaphthene	d_8-Acenaphthylene
Fluorene	d_{10}-Phenanthrene
Phenanthrene	d_{10}-Phenanthrene
Anthracene	d_{10}-Phenanthrene
Fluoranthene	d_{10}-Fluoranthene
Pyrene	d_{10}-Fluoranthene
Benzo(a)anthracene	d_{12}-Benzo(a)anthracene
Chrysene	d_{12}-Chrysene
Benzo(b)fluoranthene	d_{12}-Benzo(b)fluoranthene
Benzo(k)fluoranthene	d_{12}-Benzo(k)fluoranthene
Benzo(e)pyrene	d_{12}-Benzo(a)pyrene
Benzo(a)pyrene	d_{12}-Benzo(a)pyrene
Perylene	d_{12}-Perylene
Indeno(1,2,3-cd)pyrene	d_{12}-Indeno(1,2,3,c-d)pyrene
Dibenz(a,h)anthracene	d_{14}-Dibenz(a,h)anthracene
Benzo(ghi)perylene	d_{12}-Benzo(ghi)perylene
Surrogate Standards	
d_{10}-Fluorene	d_{10}-Phenanthrene
d_{14}-Terphenyl	d_{10}-Fluoranthene

TABLE 11A

ASSIGNMENTS OF INTERNAL STANDARDS FOR CALCULATION OF RRFs AND QUANTITATION OF TARGET PAHs AND SURROGATE STANDARDS USING ALTERNATIVE HRMS SPIKING SCHEME

Analyte	Internal Standards
Unlabeled PAH	
Naphthalene	d_8-Naphthalene
2-Methylnaphthalene	d_{10}-Acenaphthene
Acenaphthylene	d_8-Acenaphthylene
Acenaphthene	d_{10}-Acenaphthene
Fluorene	d_{10}-Fluorene
Phenanthrene	d_{10}-Phenanthrene
Anthracene	d_{10}-Phenanthrene
Fluoranthene	d_{10}-Fluoranthene
Pyrene	d_{10}-Fluoranthene
Benzo(a)anthracene	d_{12}-Benzo(a)anthracene
Chrysene	d_{12}-Chrysene
Benzo(b)fluoranthene	d_{12}-Benzo(b)fluoranthene
Benzo(k)fluoranthene	d_{12}-Benzo(k)fluoranthene
Benzo(e)pyrene	d_{12}-Benzo(a)pyrene
Benzo(a)pyrene	d_{12}-Benzo(a)pyrene
Perylene	d_{12}-Benzo(a)pyrene
Indeno(1,2,3-cd)pyrene	d_{12}-Indeno(1,2,3,c-d)pyrene
Dibenz(a,h)anthracene	d_{14}-Dibenz(a,h)anthracene
Benzo(ghi)perylene	d_{12}-Benzo(ghi)perylene
Surrogate Standards	
d_{14}-Terphenyl	d_{10}-Fluoranthene
d_{12}-Benzo(e)pyrene	d_{12}-Benzo(a)pyrene

TABLE 12

ASSIGNMENTS OF RECOVERY STANDARDS FOR DETERMINATION OF PERCENT RECOVERIES OF INTERNAL STANDARDS AND THE ALTERNATE STANDARD

Analyte	Recovery Standard
Internal Standards	
d_8-Naphthalene	d_{10}-Acenaphthene
d_{10}-2-Methylnaphthalene	d_{10}-Acenaphthene
d_8-Acenaphthylene	d_{10}-Acenaphthene
d_{10}-Phenanthrene	d_{10}-Pyrene
d_{10}-Fluoranthene	d_{10}-Pyrene
d_{12}-Benzo(a)anthracene	d_{10}-Pyrene
d_{12}-Chrysene	d_{10}-Pyrene
d_{12}-Benzo(b)fluoranthene	d_{12}-Benzo(e)pyrene
d_{12}-Benzo(k)fluoranthene	d_{12}-Benzo(e)pyrene
d_{12}-Benzo(a)pyrene	d_{12}-Benzo(e)pyrene
d_{12}-Perylene	d_{12}-Benzo(e)pyrene
d_{12}-Indeno(1,2,3,c-d)pyrene	d_{12}-Benzo(e)pyrene
d_{14}-Dibenz(a,h)anthracene	d_{12}-Benzo(e)pyrene
d_{12}-Benzo(ghi)perylene	d_{12}-Benzo(e)pyrene
Alternate Standard	
d_{10}-Anthracene	d_{10}-Pyrene

TABLE 12A

ASSIGNMENTS OF RECOVERY STANDARDS FOR DETERMINATION OF PERCENT RECOVERIES OF INTERNAL STANDARDS AND THE ALTERNATE STANDARD USING ALTERNATIVE HRMS SPIKING SCHEME

Analyte	Recovery Standard
Internal Standards	
d_8-Naphthalene	d_{10}-2-Methylnaphthalene
d_{10}-2-Methylnaphthalene	d_{10}-2-Methylnaphthalene
d_8-Acenaphthylene	d_{10}-2-Methylnaphthalene
d_{10}-Phenanthrene	d_{10}-Pyrene
d_{10}-Fluoranthene	d_{10}-Pyrene
d_{12}-Benzo(a)anthracene	d_{10}-Pyrene
d_{12}-Chrysene	d_{10}-Pyrene
d_{12}-Benzo(b)fluoranthene	d_{12}-Perylene
d_{12}-Benzo(k)fluoranthene	d_{12}-Perylene
d_{12}-Benzo(a)pyrene	d_{12}-Perylene
d_{12}-Perylene	d_{12}-Perylene
d_{12}-Indeno(1,2,3,c-d)pyrene	d_{12}-Perylene
d_{14}-Dibenz(a,h)anthracene	d_{12}-Perylene
d_{12}-Benzo(ghi)perylene	d_{12}-Perylene
Alternate Standard	
d_{10}-Anthracene	d_{10}-Pyrene

TABLE 13

QUANTITATION AND CONFIRMATION IONS FOR SELECTED ION MONITORING OF PAHs BY HRGC/LRMS

Analyte	Quant. Ion	Confirm. Ion	%Relative Abundance of Confirm. Ion
Naphthalene	128	127	10
d_8-Naphthalene	136	68	80
2-Methylnaphthalene	142	141	80
d_{10}-2-Methylnaphthalene	152		
Acenaphthylene	152	153	15
d_8-Acenaphthylene	160		
Acenaphthene	154	153	86
d_{10}-Acenaphthene	164		
Fluorene	166	165	80
d_{10}-Fluorene	176		
Phenanthrene	178	176	15
d_{10}-Phenanthrene	188	94	
Anthracene	178	176	15
d_{10}-Anthracene	188	94	
Fluoranthene	202	101	15
d_{10}-Fluoranthene	212	106	
Pyrene	202	101	15
d_{10}-Pyrene	212	106	
Benzo(a)anthracene	228	114	15
d_{12}-Benzo(a)anthracene	240	120	
Chrysene	228	114	15
d_{12}-Chrysene	240	120	
d_{14}-Terphenyl	244	122	15

TABLE 13 (CONT)

QUANTITATION AND CONFIRMATION IONS FOR SELECTED
ION MONITORING OF PAHs BY HRGC/LRMS

Analyte	Quant. Ion	Confirm. Ion	%Relative Abundance of Confirm. Ion
Benzo(b)fluoranthene	252	126	25
d_{12}-Benzo(b)fluoranthene	264	132	
Benzo(k)fluoranthene	252	126	25
d_{12}-Benzo(k)fluoranthene	264	132	
Benzo(e)pyrene	252	126	25
d_{12}-Benzo(e)pyrene	264	132	
Benzo(a)pyrene	252	126	25
d_{12}-Benzo(a)pyrene	264	132	
Perylene	252	126	26
d_{12}-Perylene	264	132	
Indeno(1,2,3-cd)pyrene	276	138	28
d_{12}-Indeno(1,2,3-cd)pyrene	288		
Dibenz(ah)anthracene	278	139	24
d_{14}-Dibenz(ah)anthracene	292		
Benzo(ghi)perylene	276	138	37
d_{12}-Benzo(ghi)perylene	288		

TABLE 14

MASS DESCRIPTORS USED FOR SELECTED ION MONITORING FOR HRGC/HRMS

Descriptor No.	Analyte Type	Ion m/z	Accurate
1	Naphthalene	M	128.0626
	PFK	LOCK	130.9920
	d_8-Naphthalene	IS	136.1128
	2-Methylnaphthalene	M	142.0782
	d_{10}-2-Methylnaphthalene	IS	152.1410
	Acenaphthylene	M	152.0626
	d_8-Acenaphthylene	IS	160.1128
	Acenaphthene	M	154.0782
	d_{10}-Acenaphthene	RS	164.1410
	PFK	QC	169.9888
2	Fluorene	M	166.0782
	d_{10}-Fluorene	SS	176.1410
	Phenanthrene	M	178.0782
	d_{10}-Phenanthrene	IS	188.1410
	Anthracene	M	178.0782
	d_{10}-Anthracene	AS	188.1410
	Fluoranthene	M	202.0782
	d_{10}-Fluoranthene	IS	212.1410
	Pyrene	M	202.0782
	PFK	QC	204.9888
	d_{10}-Pyrene	RS	212.1410
	Benzo(a)anthracene	M	228.0939
	d_{12}-Benzo-a-Anthracene	IS	240.1692
	Chrysene	M	228.0939
	d_{12}-Chrysene	IS	240.1692
	PFK	LOCK	230.9856
	d_{14}-Terphenyl	SS	244.1974

IS   = Internal Standard
SS   = Surrogate Standard
AS   = Alternate Standard
RS   = Recovery Standard
LOCK = Lock-Mass Ion
QC   = Quality Control Check Ion

TABLE 14 (CONT)

MASS DESCRIPTORS USED FOR SELECTED ION MONITORING FOR HRGC/HRMS

Descriptor No.	Analyte Type	Ion m/z	Accurate
3	Perylene	M	252.0939
	d_{12}-Perylene	IS	264.1692
	PFK	QC	268.9824
	Benzo(b)fluoranthene	M	252.0939
	d_{12}-Benzo(b)fluoranthene	IS	264.1692
	Benzo(k)fluoranthene	M	252.0939
	d_{12}-Benzo-k-fluoranthene	IS	264.1692
	Benzo(e)pyrene	M	252.0939
	d_{12}-Benzo(e)pyrene	RS	264.1692
	Benzo(a)pyrene	M	252.0939
	d_{12}-Benzo(a)pyrene	IS	264.1692
	Benzo(ghi)perylene	M	276.0939
	d_{12}-Benzo(ghi)perylene	IS	288.1692
	Indeno(1,2,3-cd)pyrene	M	276.0939
	d_{12}-Indeno(1,2,3-cd)pyrene	IS	288.1692
	Dibenzo(ah)anthracene	M	278.1096
	PFK	LOCK	280.9824
	d_{14}-Dibenzo(ah)anthracene	IS	292.1974

The following nuclidic masses were used:

$H = 1.007825$ $\qquad$ $^2H = 2.014102$ $\qquad$ $C = 12.000000$

IS   =   Internal Standard
SS   =   Surrogate Standard
AS   =   Alternate Standard
RS   =   Recovery Standard
LOCK =   Lock-Mass Ion
QC   =   Quality Control Check Ion

FIGURE 1

METHOD 429 FLOWCHART

34

| §1.3.9 | *The end user is identified* |
| §1.3.10 | *The tester is designated* |

35

| | *The end user chooses:* |
| §2.1.1 | ǀ source target concentration |

36

§2.1.2	*The tester selects analyst with documented*
§8.4	*experience in satisfactory performance of analytical*
§8.4.1	*procedures*

37

	Tester and laboratory coordinate:
§4.3.2	ǀ pre-test cleaning of glassware
§4.2	ǀ pre-test cleaning, contamination checks, and
§4.3.3	storage of sampling materials and reagents
§4.3.4	ǀ preparation of filter, sorbent cartridges, method blanks, and LCS

38

	Tester requests pre-test analytical results from laboratory:
§10.1.1	ǀ contamination check of filters
§10.1.2	ǀ contamination check of XAD-2 resin
§10.1.3	ǀ Method detection limits (MDLs) and Practical quantitation limits (PQLs)

39

	Tester calculates and plans:
§2.5	ǀ ≥3 sampling runs and ≥1 blank sampling train
	ǀ sample volume
	ǀ sampling time
	ǀ source reporting limit
	ǀ chain of custody

40

| | *Tester performs:* |
| §4.3.1 | ǀ calibration of equipment |

41

| | *Tester writes:* |
| §2.2 | ǀ pre-test protocol |

42

	Tester performs:
§4.4.1	ǀ preliminary field sampling determinations
§4.4.2	ǀ sampling train preparation
§4.4.3	ǀ leak-checks
§4.4.4	ǀ sampling procedure
	ǀ ≥3 sampling runs
	ǀ ≥1 blank sampling train
§5	ǀ recovery of all runs and blank sampling train

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	Tester delivers:
§5.3	ǀ recovered sampling runs and blank train(s)
§5.4	ǀ chain of custody record

44

	Laboratory performs:
§6	ǀ extraction of field samples
§7	ǀ analyses
§8	ǀ QA/QC procedures
§9	ǀ chain of custody
§10.2	ǀ reporting requirements

45

	Tester performs:
§4.3.1	ǀ post-test calibrations
§9.2	ǀ calculations
§10.3	ǀ data recording and chain of custody
	ǀ reporting requirements
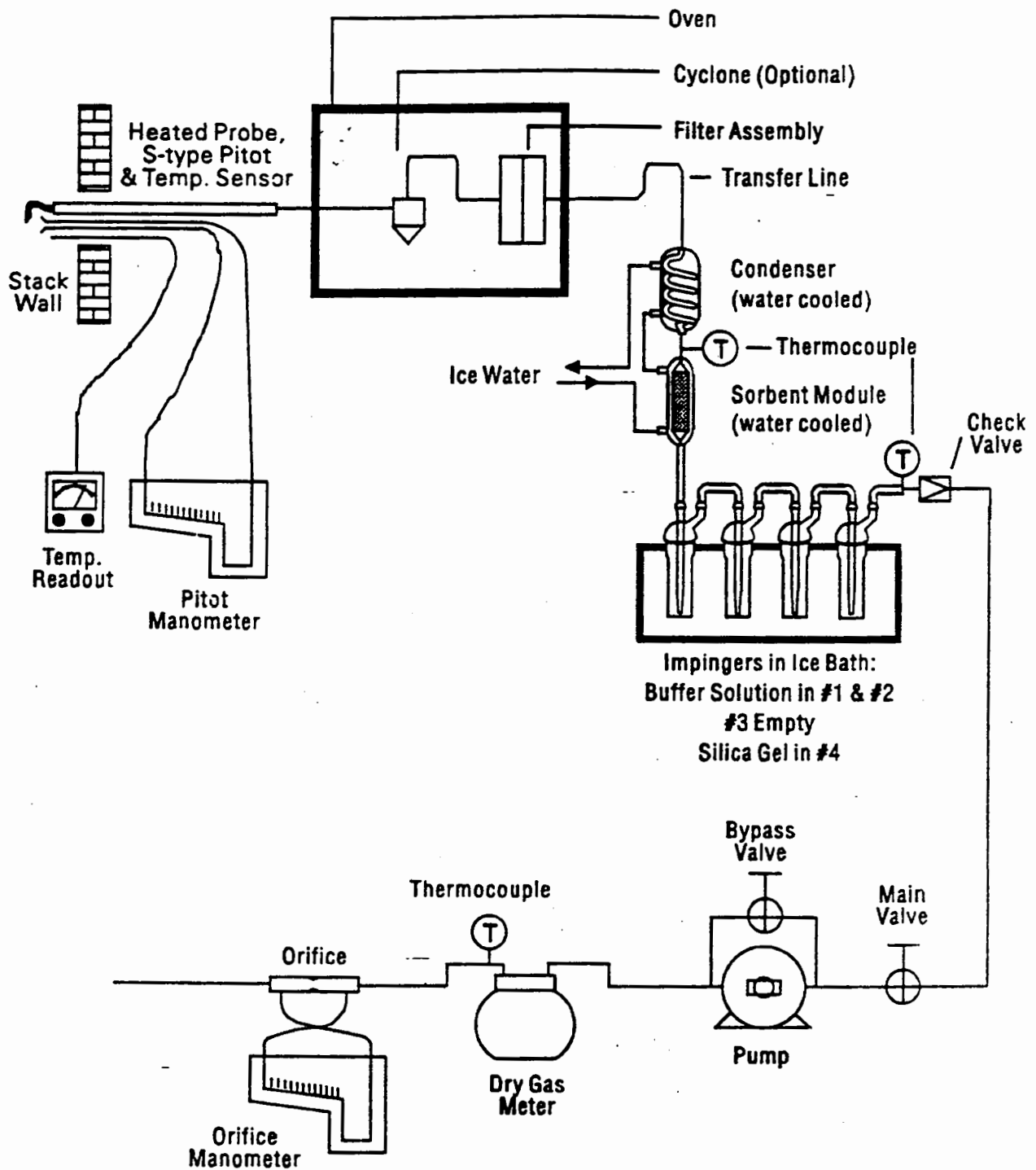
Figure 2

PAH Sampling Train
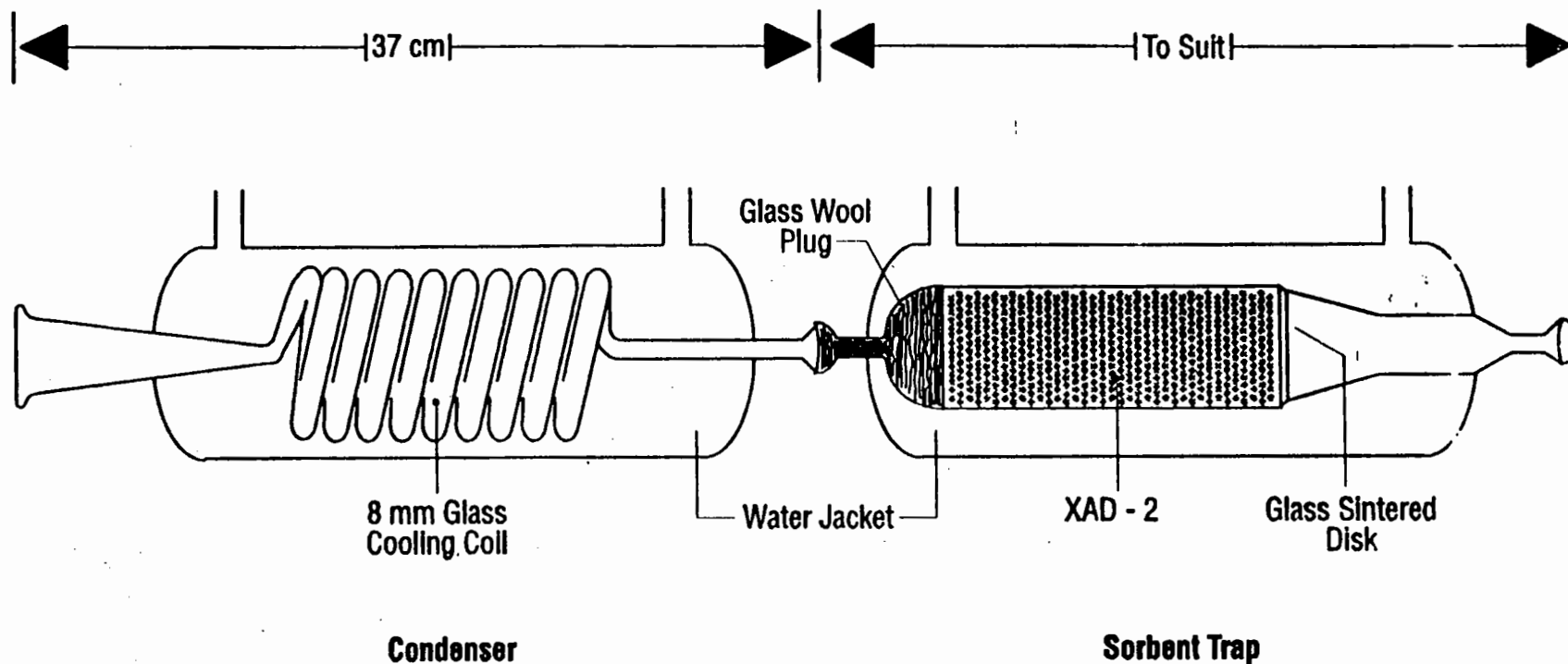
Figure 3

Condenser and Sorbent Trap for Collection
of Gaseous PAHs
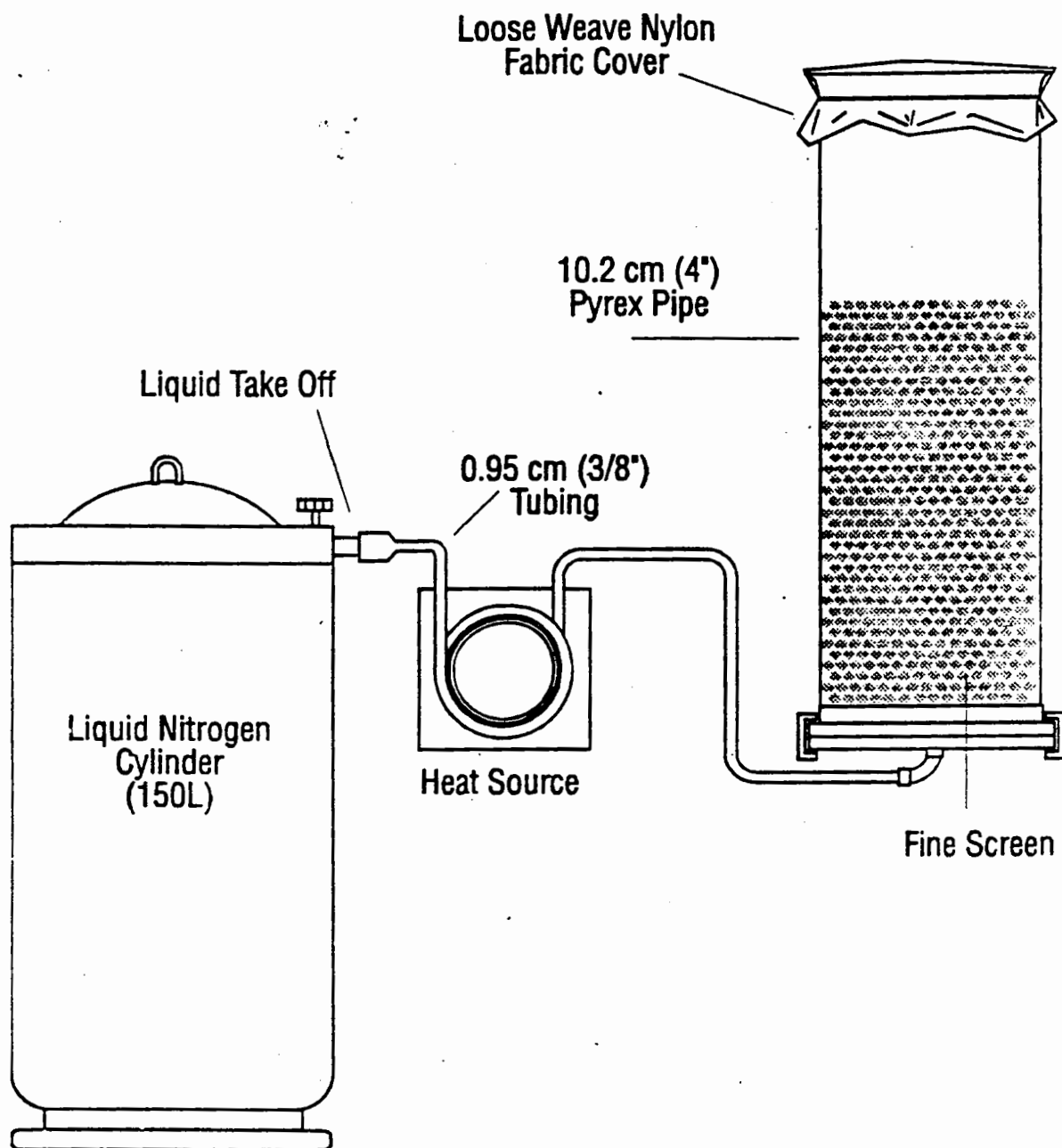
Figure 4

XAD-2 Fluidized Bed Drying Apparatus

FIGURE 5

METHOD 429 FIELD DATA RECORD

Run No. _____

Location _____

Date _____

Operator_____

Meter Box No. _____

Local Time

 Start/Stop _____

$\Delta H@$ _____

Stack Diameter _____

Meter Box Calibration

Factor (Y) _____

Pitot Tube Factor _____

Probe Tip Dia, in. _____

Probe Length _____

Sampling Train Leak Test   Leak Rate

Before _____ in. Hg _____ cu.ft/min

After _____ in. Hg _____ cu.ft/min

Leak-Check Volume _____ cu. ft.

Pitot Tube Leak-Check

Before _____ After _____

Project No. _____

Plant Name _____

Ambient Temp °F _____

Meter Temp °F _____

Bar. Press, "Hg _____

Stack Press, "H_2O _____

Assumed Moisture, % _____

Heater Box Setting, °F _____

Probe Heater Setting, °F _____

Assumed M.W. (wet%) _____

Assumed M.W. (dry%) _____

Sampling Point	Clock Time	Dry Gas Meter, cu, ft.	Pitot ΔP in. H_2O	Orifice ΔH "H_2O		Temperature (°F)			Pump Vacuum in. Hg
				Desired	Actual	Impinger	Filter box	Stack	
Start									

Figure 6

Recovery of PAH Sampling Train

Column 1:

Rinse with known volume:
1. acetone
2. methylene chloride
3. hexane

→ Nozzle and Probe Liner

→ Front half filter holder

→ Container No. 1

Mark liquid level, Store at 4°C or lower away from light

Column 2:

Transfer

→ Filter

→ Container No. 2

Store at 4°C or lower away from light

Column 3:

Rinse with known volume:
1. acetone
2. methylene chloride
3. hexane

→ Filter support, Back half filter holder

→ Transfer line

→ Condenser

→ Container No. 3

Mark liquid level, Store at 4°C or lower away from light

Column 4:

Cap

→ Resin cartridge

→ Resin cartridge

Store at 4°C or lower away from light

Column 5:

A. Tare weigh Container #4
B. Decant contents of impingers into tared Container #4

Impinger No. 1   Impinger No. 2   Impinger No. 3

→ Container No. 4

C. Weigh Container #4
D. Mark liquid level, Store at 4°C or lower away from light

Rinse with known volume:
1. acetone
2. methylene chloride
3. hexane

Impinger No. 1   Impinger No. 2   Impinger No. 3

→ Container No. 5

Mark liquid level, Store at 4°C or lower away from light

Column 6:

A. Tare weigh cartridge with silica gel
B. Weigh after sampling

→ Silica gel cartridge

→ Recycle

Figure 7

Flow Chart for Sampling, Extraction and Cleanup for Determination of PAH in a Split Sample

[1]Containers No. 1 and No. 3
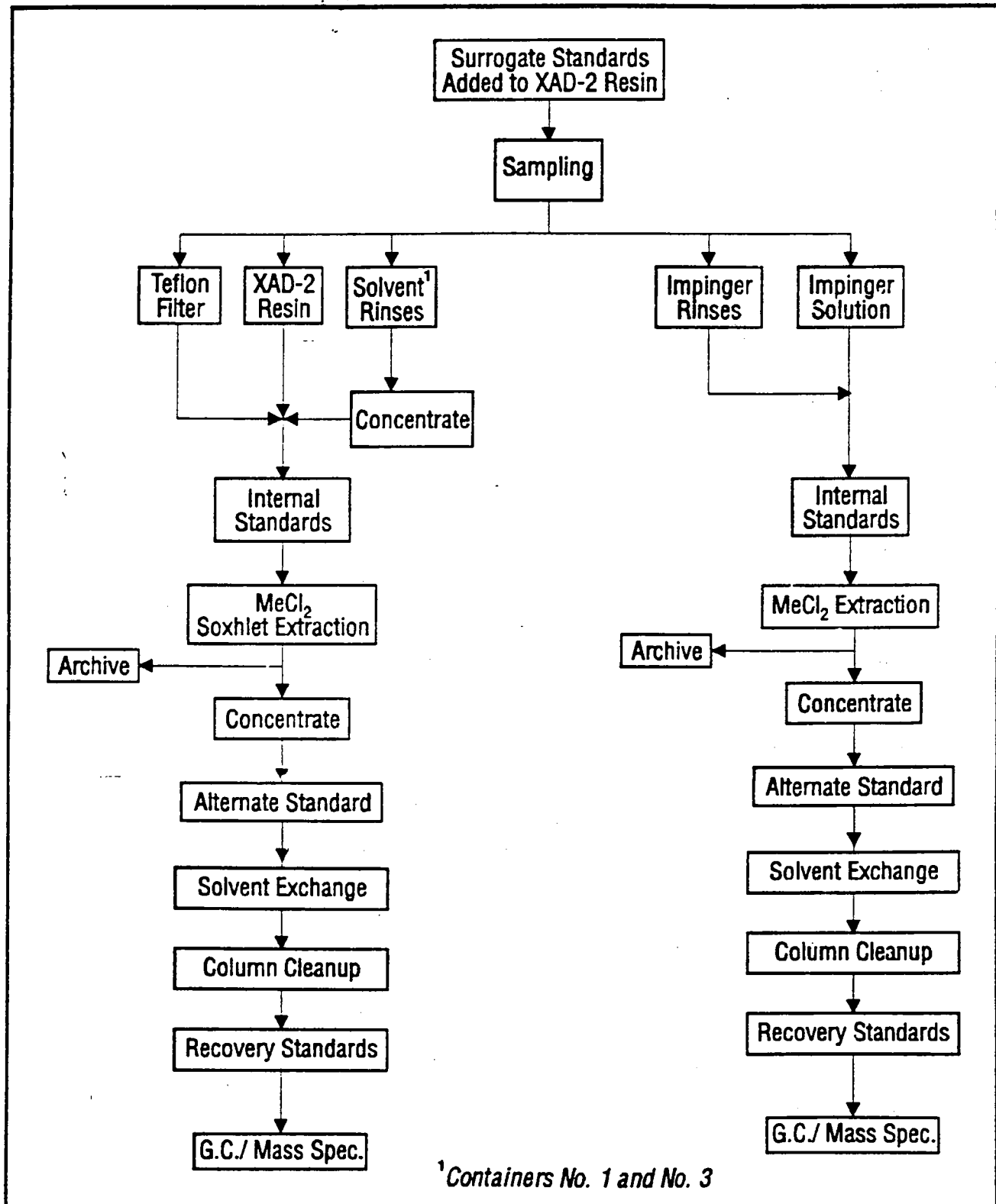
Figure 8
Flow Chart for Sampling, Extraction and Cleanup for Determination of PAH in a Composite Sample
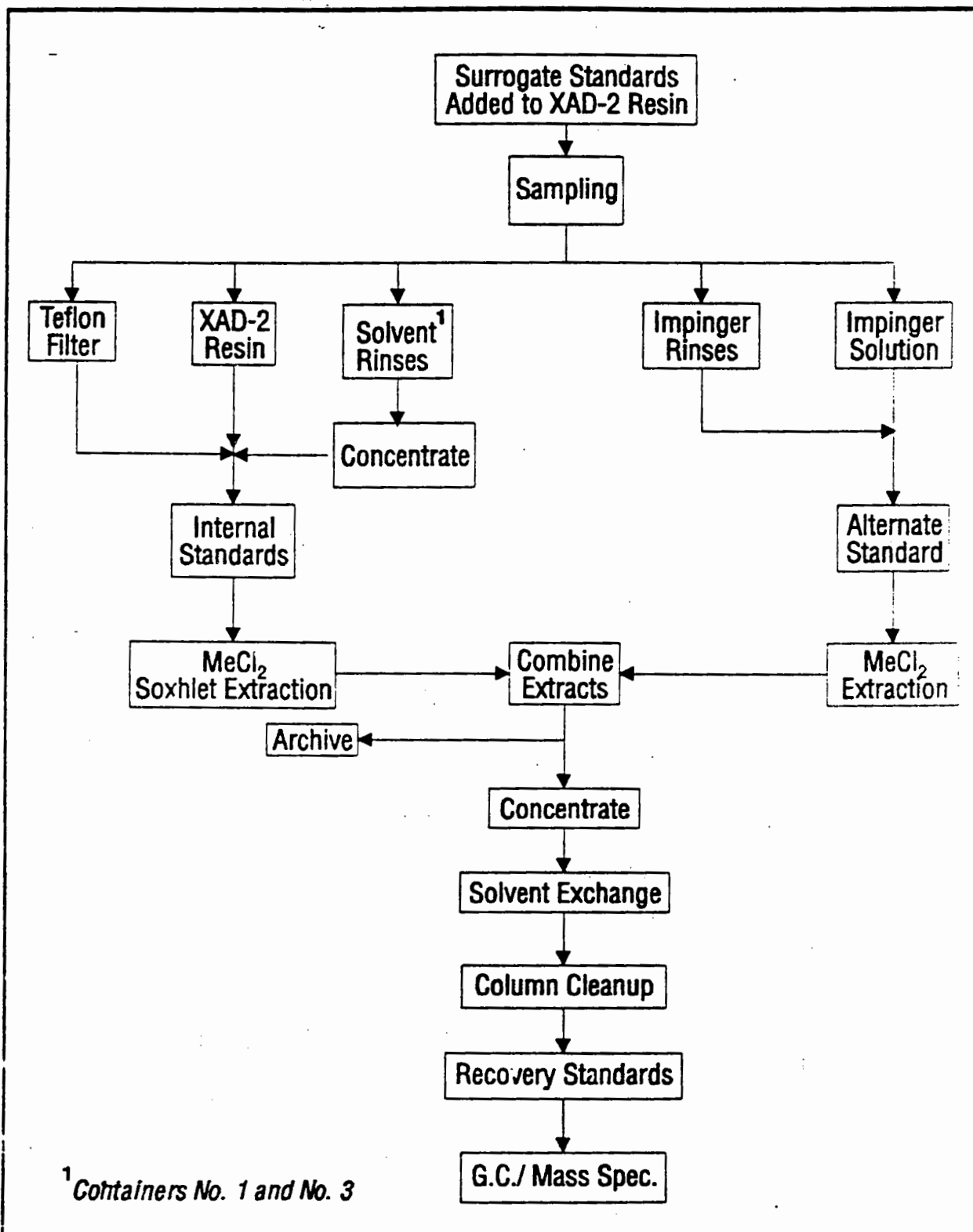
FIGURE 9

EXAMPLE OF PRE-TEST CALCULATIONS FOR PAH EMISSIONS TEST

	PQL (ng/sample)	STC (ng/dscm)	MSV (dscf)	MST (hours)	F	SRL (ng/dscm)
					PST = 6 hours	
					PSV = 180 dscf	
Naphthalene	2400	<1500	>56.5	>1.89	NA	471
2-Methylnaphthalene	330	NA	NA	NA	NA	64.7
Acenaphthylene	5.0	180	0.98	0.03	183	0.98
Acenaphthene	5.0	6	29.4	0.98	6	0.98
Fluorene[1]	83	<6	>489	>16.3	NA	16.3
Phenanthrene	110	120	32.4	1.08	6	21.6
Anthracene	5.0	<6	>29.4	>0.98	NA	0.98
Fluoranthene	5.0	46	3.8	0.13	47	0.98
Pyrene	5.0	46	3.8	0.13	47	0.98
Benzo(a)anthracene	5.0	<6	>29.4	>0.98	NA	0.98
Chrysene	5.0	42	4.2	0.14	43	0.98
Benzo(b)fluoranthene	5.0	50	3.5	0.12	51	0.98
Benzo(k)fluoranthene	5.0	50	3.5	0.12	51	0.98
Benzo(e)pyrene	5.0	NA	NA	NA	NA	0.98
Benzo(a)pyrene	5.0	<6	>29.4	>0.98	NA	0.98
Perylene	5.0	NA	NA	NA	NA	0.98
Indeno(1,2,3-c,d)pyrene	5.0	<6	>29.4	>0.98	NA	0.98
Dibenzo(a,h)anthracene	5.0	<6	>29.4	>0.98	NA	0.98
Benzo(g,h,i)perylene	5.0	<6	>29.4	>0.98	NA	0.98

Average Volumetric Sampling Rate (VSR) = 0.5 dscfm = 30 dscf/hr

PQL = Practical quantitation limit for analyte (based on pre-test analysis of XAD-2 resin)

STC = Source target concentration for analyte. (From previous emissions test. Samples were analyzed by HRGC/LRMS).

MSV = Minimum sample volume required to collect detectable levels of target analyte.
(MSV = PQL ÷ STC) *Equation 429-1*

MST = Minimum sample time required to collect detectable levels of target analyte at VSR.
(MST = MSV ÷ VSR) *Equation 429-2*

PST = Planned sampling time (6 hours chosen as the longest practical sampling time for the planned emissions test)

PSV = Planned sample volume (PSV = PST × VSR) *Equation 429-4*

F = Safety factor (>1) that allows for deviation from ideal sampling and analytical conditions. (F = PSV ÷ MSV) *Equation 429-5*

SRL = Source reporting limit if the target analyte cannot be detected with the planned test parameters. (SRL = PQL ÷ PSV) *Equation 429-7*

NA = This calculation is not applicable either because there is no STC value available or the STC is a detection limit.

[1] PSV is lower than the MSV. Therefore, the analyte is not expected to be detected if it is present at the target concentrations. It will only be detected if the actual concentration is higher than the indicated SRL.

FIGURE 10

CARB METHOD 429 (PAHs) SAMPLING TRAIN SET-UP RECORD

RUN NO. _____ PROJECT NO. _____
PLANT NAME _____ PLANT LOCATION _____
SET-UP DATE _____ SET-UP BY _____
RECEIVED BY _____ DATE/TIME _____

	COMPONENTS	COMPONENT ID	OTHER INFORMATION	
1.	NOZZLE	_____	Material	_____
			Diameter	_____
2.	PROBE	_____	Liner material	_____
			Length	_____
3.	FILTER HOLDER	_____	Before set-up, all .openings sealed with	_____
			Filter support type	_____
4.	FILTER	Lot # _____	Filter Type	_____
			Size	_____
			Contamination check?	_____
5.	TRANSFER LINE AND CONDENSER	_____	Transfer line material	_____
	Fittings	_____		_____
6.	XAD-2 RESIN CARTRIDGE	_____	Both ends sealed in lab prior to set-up	_____
			Fittings	_____
			Contamination check?	_____
			Spiked?	_____
7.	IMPINGERS: No. 1 U-Connector	_____ _____	Charge with 100 ml. impinger solution and weigh	_____ g
	No. 2 U-Connector	_____ _____	Charge with 100 mL impinger solution and weigh	_____ g
	No. 3 U-Connector	_____ _____	Weigh empty	_____ g
8.	SILCA GEL CARTRIDGE	_____	Tare weight	_____ g

Appearance _____

FIGURE 11

CARB METHOD 429 (PAHs) SAMPLING TRAIN RECOVERY RECORD

RUN NO. _____   PROJECT NO. _____
PLANT NAME _____   PLANT LOCATION _____
RECOVERY DATE _____   RECOVERED BY _____

1. **CHECK** whether openings were covered. **RINSE 3x** each with **Acetone, MeCl₂, Hexane. MARK** liquid level and **STORE** containers at temp. **<4°C** away from light.

Component	Openings covered?	Rinse volume (mL) Acetone	MeCl₂	Hexane	Storage Container(s) IDs
Nozzle					
Probe liner					
Filter holder front					

2. **STORE** filter(s) at temp. **<4°C** away from light.   **RECORD ALL** sample storage information.

Component	Appearance after sampling	Storage (Temperature & light)	Storage Container(s) ID
Filter			
Filter			
Filter			

3. **CHECK** whether openings were covered.   **RINSE 3x** each with **Acetone, MeCl₂, Hexane. MARK** liquid level and **STORE** containers at temp. **<4°C** away from light.

Component	Openings covered?	Rinse volume (mL) Acetone	MeCl₂	Hexane	Storage Temp. & light	Storage Container ID
Filter support and filter holder back						
Transfer line						
Condenser						

4. **STORE** Resin cartridges at temp. **<4°C** away from light.   **RECORD ALL** storage information.

ID	Appearance after sampling	Storage temperature & light conditions

5. **WEIGH** impinger contents and silica gel cartridge. **MARK** liquid level and **STORE** impinger contents at temp. **<4°C** away from light.

Weight	No. 1	No. 2	No. 3	Additional impingers No. 4	No. 5	Silica gel cartridge
Final (g)						
Before sampling (g)						
Gain (g)	(A) ____	(B) ____	(C) ____	(D) ____	(E) ____	(F) ____

Total condensate (A) + (B) + (C) + (D) + (E) + (F) _____ (g)

STORAGE CONTAINER ID(s) ____ ____ ____ ____

6. **RINSE** impingers 3x each with **Acetone, MeCl₂, Hexane. MARK** liquid level and **STORE** impinger rinses at temp. **<4°C** away from light.

Rinse volumes (mL)	Acetone				
	MeCl₂				
	Hexane				
STORAGE CONTAINER ID(s)					

FIGURE 12

CHAIN OF CUSTODY SAMPLE RECORD

Project # _____ Date:_____ Start: _____

Stop: _____

Source name: _____ Sample/Run # : _____

Sampling location: _____ Sample type: _____

Chain of Custody Log Record # (s) _____ Operator: _____

SAMPLE STORAGE INFORMATION

SAMPLE PRESERVATION	Comments
Ice/Dry ice?	

CHAIN OF CUSTODY

ACTION	DATE	TIME	GIVEN BY	TAKEN BY

RELATED IDs	DESCRIPTION/COMMENTS	Log #s
FR	Front rinse (nozzle, probe,filter holder front)	
F	Filter in sealed storage container	
BB	Back rinse (filter support. filter holder. sample line & condenser	
C	Resin cartridge	
I	Impinger contents	
IR	Impinger rinses	

FIGURE 13

CHAIN OF CUSTODY LOG RECORD

PROJECT NO. _____   Page _____ of _____

Log #	Sample ID	Date	Time	Comments	Given by	Taken by

Sample Identifier   **Sample Description**

FR   Rinses of probe and front half of filter holder
F   Filter in sealed storage container
BR   Rinses of filter support, back half of filter holder, sample transfer line and condenser
C   Aluminum foil wrapped, capped resin cartridge
I   Impinger contents
IR   Impinger rinses

EXAMPLE GC/MS SUMMARY REPORT (HRMS) FOR INITIAL CALIBRATION SOLUTION #1
CALIFORNIA AIR RESOURCES BOARD METHOD 429 POLYCYCLIC AROMATIC HYDROCARBONS

ICAL ID: ST1120A1   ACQUIRED: 12/3/94 16:23:24   INSTRUMENT: W
RUN #: PAHCS1   PROCESSED: 12/3/94   OPERATOR: MPA

	RT.	RRT	Area	RRF
Naphthalene	8:20	1.006	6.66 E+07	0.75
2-Methylnaphthalene	9:42	1.007	1.44 E+07	1.30
Acenaphthylene	11:04	1.003	1.57 E+07	1.44
Acenaphthene	11:20	1.004	1.05 E+07	0.94
Fluorene	12:06	1.003	8.15 E+06	1.05
Phenanthrene	13:20	1.003	1.99 E+07	1.15
Anthracene	13:23	1.001	7.07 E+06	1.02
Fluoranthene	14:38	1.001	3.18 E+07	1.26
Pyrene	14:55	1.001	3.31 E+07	1.31
Benzo(a)anthracene	16:34	1.002	2.08 E+07	1.13
Chrysene	16:39	1.003	2.26 E+07	1.13
Benzo(b)fluoranthene	18:54	1.004	2.35 E+07	1.69
Benzo(k)fluoranthene	18:58	1.004	2.50 E+07	1.24
Benzo(e)pyrene	19:42	1.004	2.41 E+07	1.20
Benzo(a)pyrene	19:51	1.003	2.11 E+07	1.07
Perylene	20:06	1.004	1.38 E+07	0.70
Indeno(1,2,3-c,d)pyrene	23:60	1.006	2.07 E+07	2.19
Dibenzo(a,h)anthracene	24:01	1.006	1.49 E+07	1.66
Benzo(g,h,i)perylene	25:15	1.005	1.84 E+07	2.23
d_8-Naphthalene	8:17	1.000	3.54 E+08	4.22
d_8-Acenaphthylene	11:02	1.000	1.09 E+08	1.29
d_{10}-Acenaphthene	11:17	1.000	1.11 E+08	1.32
d_{10}-Fluorene	12:04	1.000	7.78 E+07	0.93
d_{10}-Phenanthrene	13:18	1.000	6.92 E+07	0.82
d_{10}-Fluoranthene	14:37	1.000	2.53 E+08	1.03
d_{12}-Benzo(a)anthracene	16:32	1.000	1.83 E+08	0.75
d_{12}-Chrysene	16:36	1.000	2.00 E+08	0.82
d_{12}-Benzo(b)fluoranthene	18:50	1.000	2.77 E+08	1.35
d_{12}-Benzo(k)fluoranthene	18:54	1.000	4.03 E+08	1.95
d_{12}-Benzo(a)pyrene	19:47	1.000	3.93 E+08	1.91
d_{12}-Indeno(1,2,3-c,d)pyrene	23:52	1.000	1.89 E+08	0.92
d_{14}-Dibenzo(a,h)anthracene	23:52	1.000	1.80 E+08	0.87
d_{12}-Benzo(g,h,i)perylene	25:07	1.000	1.65 E+08	0.80
d_{14}-Terphenyl	14:59		2.65 E+08	0.52
d_{12}-Benzo(e)pyrene	19:37	1.000	1.44 E+08	0.37
d_{10}-Anthracene	13:22	1.000	5.82 E+07	0.69
d_{10}-2-Methylnaphthalene	9:38	1.000	8.40 E+07	—
d Pyrene	14:54	1.000	2.45 E+08	—
d_{12}-Perylene	20:01	1.000	1.03 E+08	—

EXAMPLE OF INITIAL CALIBRATION (ICAL) RRF SUMMARY
CALIFORNIA AIR RESOURCES BOARD METHOD 429 POLYCYCLIC AROMATIC HYDROCARBONS

ICAL ID: ST1120   ACQUIRED: 3-DEC-94   INSTRUMENT. W
RUN #: NA   PROCESSED: 3-DEC-94   OPERATOR: MPA

	RRF #1	RRF #2	RRF #3	RRF #4	RRF #5	Mean RRF	SD	%RSD
Naphthalene	0.75	0.66	0.61	0.64	0.71	0.67	0.056	8.29%
2-Methylnaphthalene	1.30	1.15	1.10	1.12	1.26	1.19	0.089	7.47%
Acenaphthylene	1.44	1.27	1.24	1.28	1.43	1.33	0.096	7.19%
Acenaphthene	0.94	0.84	0.80	0.83	0.94	0.87	0.067	7.72%
Fluorene	1.05	0.94	0.88	0.92	1.07	0.97	0.082	8.43%
Phenanthrene	1.15	1.06	1.01	1.05	1.23	1.10	0.088	8.00%
Anthracene	1.02	1.00	0.98	0.95	1.14	1.02	0.074	7.25%
Fluoranthene	1.26	1.15	1.08	1.13	1.28	1.18	0.085	7.21%
Pyrene	1.31	1.27	1.13	1.15	1.41	1.25	0.115	9.22%
Benzo(a)anthracene	1.13	1.05	1.05	1.04	1.23	1.10	0.082	7.43%
Chrysene	1.13	1.02	0.97	0.98	1.11	1.04	0.073	7.00%
Benzo(b)fluoranthene	1.69	1.45	1.46	1.42	1.86	1.58	0.194	12.33%
Benzo(k)fluoranthene	1.24	1.25	1.14	1.18	1.26	1.21	0.052	4.32%
Benzo(e)pyrene	1.20	1.12	1.06	1.06	1.19	1.12	0.066	5.89%
Benzo(a)pyrene	1.07	0.99	0.96	0.96	1.14	1.02	0.080	7.81%
Perylene	0.70	0.63	0.58	0.60	0.70	0.64	0.059	9.12%
Indeno(1,2,3-c,d)pyrene	2.19	2.01	1.92	1.99	2.26	2.07	0.143	6.90%
Dibenzo(a,h)anthracene	1.66	1.60	1.56	1.61	1.87	1.66	0.122	7.35%
Benzo(g,h,i)perylene	2.23	2.05	1.96	2.00	2.32	2.11	0.154	7.28%
d_8-Naphthalene	4.22	4.15	4.16	4.18	4.10	4.16	0.044	1.05%
d_8-Acenaphthylene	1.29	1.29	1.28	1.27	1.30	1.29	0.012	0.91%
d_{10}-Acenaphthene	1.32	1.34	1.32	1.30	1.32	1.32	0.013	1.00%
d_{10}-Fluorene	0.93	0.95	0.94	0.95	0.95	0.94	0.011	1.21%
d_{10}-Phenanthrene	0.82	0.82	0.82	0.86	0.88	0.81	0.026	3.09%
d_{10}-Fluoranthene	1.03	1.00	1.07	1.07	0.99	1.03	0.038	3.71%
d_{12}-Benzo(a)anthracene	0.75	0.70	0.70	0.72	0.70	0.71	0.022	3.09%
d_{12}-Chrysene	0.82	0.79	0.81	0.83	0.84	0.82	0.021	2.56%
d_{12}-Benzo(b)fluoranthene	1.35	1.39	1.46	1.27	1.32	1.36	0.072	5.32%
d_{12}-Benzo(k)fluoranthene	1.95	1.95	2.14	1.84	2.11	2.00	0.124	6.23%
d_{12}-Benzo(a)pyrene	1.91	1.96	2.11	1.82	1.99	1.96	0.107	5.46%
d_{12}-Indeno(1,2,3-c,d)pyrene	0.92	0.88	0.98	0.85	0.98	0.92	0.059	6.40%
d_{14}-Dibenzo(a,h)anthracene	0.87	0.84	0.91	0.78	0.89	0.86	0.049	5.71%
d_{12}-Benzo(g,h,i)perylene	0.80	0.76	0.83	0.73	0.80	0.78	0.042	5.36%
d_{14}-Terphenyl	0.52	0.52	0.49	0.48	0.51	0.51	0.018	3.59%
d_{12}-Benzo(e)pyrene	0.37	0.37	0.37	0.36	0.36	0.36	0.005	1.50%
d_{10}-Anthracene	0.69	0.73	0.74	0.80	0.90	0.77	0.080	10.40%
d_{10}-2-Methylnaphthalene	—	—	—	—	—	—	—	—
d_{10}-Pyrene	—	—	—	—	—	—	—	—
d_{12}-Perylene	—	—	—	—	—	—	—	—

EXAMPLE OF CONTINUING CALIBRATION (CONCAL) SUMMARY
CALIFORNIA AIR RESOURCES BOARD METHOD 429 POLYCYCLIC AROMATIC HYDROCARBONS

CONCAL ID: CC1202   ICAL ID: ST1120   INSTRUMENT: W
CONCAL DATE: 12/3/94   ICAL DATE: 3-DEC-94   OPERATOR: MPA

	RRF	ICAL RRF	ΔRRF	RPD %
Naphthalene	0.68	0.67	0.01	1.5
2-Methylnaphthalene	1.42	1.19	0.23	17.6
Acenaphthylene	1.42	1.33	0.09	6.6
Acenaphthene	0.91	0.87	0.04	4.5
Fluorene	0.98	0.97	0.01	1.0
Phenanthrene	1.10	1.10	0.00	0.0
Anthracene	0.98	1.02	-0.04	4.0
Fluoranthene	1.12	1.18	-0.06	5.2
Pyrene	1.18	1.25	-0.07	5.8
Benzo(a)anthracene	1.08	1.10	-0.02	1.8
Chrysene	1.04	1.04	0.00	0.0
Benzo(b)fluoranthene	1.46	1.58	-0.12	7.9
Benzo(k)fluoranthene	1.12	1.21	-0.09	7.7
Benzo(e)pyrene	1.04	1.12	-0.08	7.4
Benzo(a)pyrene	0.95	1.02	-0.07	7.1
Perylene	0.62	0.64	-0.02	3.2
Indeno(1,2,3-c,d)pyrene	2.04	2.07	-0.03	1.5
Dibenzo(a,h)anthracene	1.61	1.66	-0.05	3.1
Benzo(g,h,i)perylene	2.11	2.11	0.00	0.0
d_8-Naphthalene	4.78	1.16	0.68	15.3
d_8-Acenaphthylene	1.20	1.29	-0.09	7.2
d_{10}-Acenaphthene	1.25	1.32	-0.07	5.5
d_{10}-Fluorene	0.85	0.94	-0.09	10.1
d_{10}-Phenanthrene	0.79	0.81	-0.02	2.5
d_{10}-Fluoranthene	1.05	1.03	0.02	1.9
d_{12}-Benzo(a)anthracene	0.69	0.71	-0.02	2.9
d_{12}-Chrysene	0.82	0.82	0.00	0.0
d_{12}-Benzo(b)fluoranthene	1.24	1.36	-0.12	9.2
d_{12}-Benzo(k)fluoranthene	1.91	2.00	-0.09	4.6
d_{12}-Benzo(a)pyrene	1.87	1.96	-0.09	4.7
d_{12}-Indeno(1,2,3-c,d)pyrene	0.84	0.92	-0.08	9.1
d_{14}-Dibenzo(a,h)anthracene	0.80	0.86	-0.06	7.2
d_{12}-Benzo(g,h,i)perylene	0.76	0.78	-0.02	2.6
d_{14}-Terphenyl	0.50	0.51	-0.01	2.0
d_{12}-Benzo(e)pyrene	0.37	0.36	0.01	2.7
d_{10}-Anthracene	0.71	0.77	-0.06	8.1
d_{10}-2-Methylnaphthalene	—	—		
d_{10}-Perylene	—	1.000		
d_{12}-Perylene	—	1.000		

July 28, 1997

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EXAMPLE OF SUMMARY REPORT OF LCS RESULTS
CALIFORNIA AIR RESOURCES BOARD METHOD 429 POLYCYCLIC AROMATIC HYDROCARBONS

Client ID_CARB_____   Sample Matrix: XAD-2   ICAL ID: _ST1120_   Resin Lot #: _LC_130M_
Lab ID: 1412 9/LCS1/LCS2   Date Received: _NA_   ICAL DATE: 12/3/94   LCS IDs: _NA_____
Instrument: _W____   Date Extracted: 11/30/94   CONCAL ID: _NA____   LCS DATE: _NA___
Operator: __MPA____   Date Analyzed: 12/3/94   CONCAL DATE: _NA_
Reviewer: __JCM____   Sample amount: Sample   Units: __NA___

COMPOUND:	LCS1 %R	LCS2 %R	RPD %
Naphthalene	100	103	3.0
2-Methylnaphthalene	96	95	1.0
Acenaphthylene	95	97	2.1
Acenaphthene	92	94	2.2
Fluorene	94	96	2.1
Phenanthrene	93	94	1.1
Anthracene	91	89	2.2
Fluoranthene	90	92	2.2
Pyrene	87	89	2.3
Benzo(a)anthracene	87	86	1.2
Chrysene	83	89	7.0
Benzo(b)fluoranthene	92	93	1.1
Benzo(k)fluoranthene	92	95	3.2
Benzo(e)pyrene	97	99	2.0
Benzo(a)pyrene	89	92	3.3
Perylene	89	89	0.0
Indeno(1,2,3-c,d)pyrene	87	90	3.4
Dibenzo(a,h)anthracene	88	90	2.2
Benzo(g,h,i)perylene	89	91	1.2
Internal Standards (%R)			
d_8-Naphthalene	67	64	
d_8-Acenaphthylene	73	70	
d_{10}-Acenaphthene	76	75	
d_{10}-Fluorene	79	81	
d_{10}-Phenanthrene	88	93	
d_{10}-Fluoranthene	84	80	
d_{12}-Benzo(a)anthracene	96	98	
d_{12}-Chrysene	96	91	
d_{12}-Benzo(b)fluoranthene	88	85	
d_{12}-Benzo(k)fluoranthene	85	84	
d_{12}-Benzo(a)pyrene	92	90	
d_{12}-Indeno(1,2,3-c,d)pyrene	104	105	
d_{14}-Dibenzo(a,h)anthracene	96	96	
d_{12}-Benzo(g,h,i)perylene	102	103	
Alternate Standard (%R)			
d_{10}-Anthracene	83	85	

FIGURE 15B

LCS RECOVERIES FOR BENZO(a)PYRENE

8/18/92 - 5/21/93
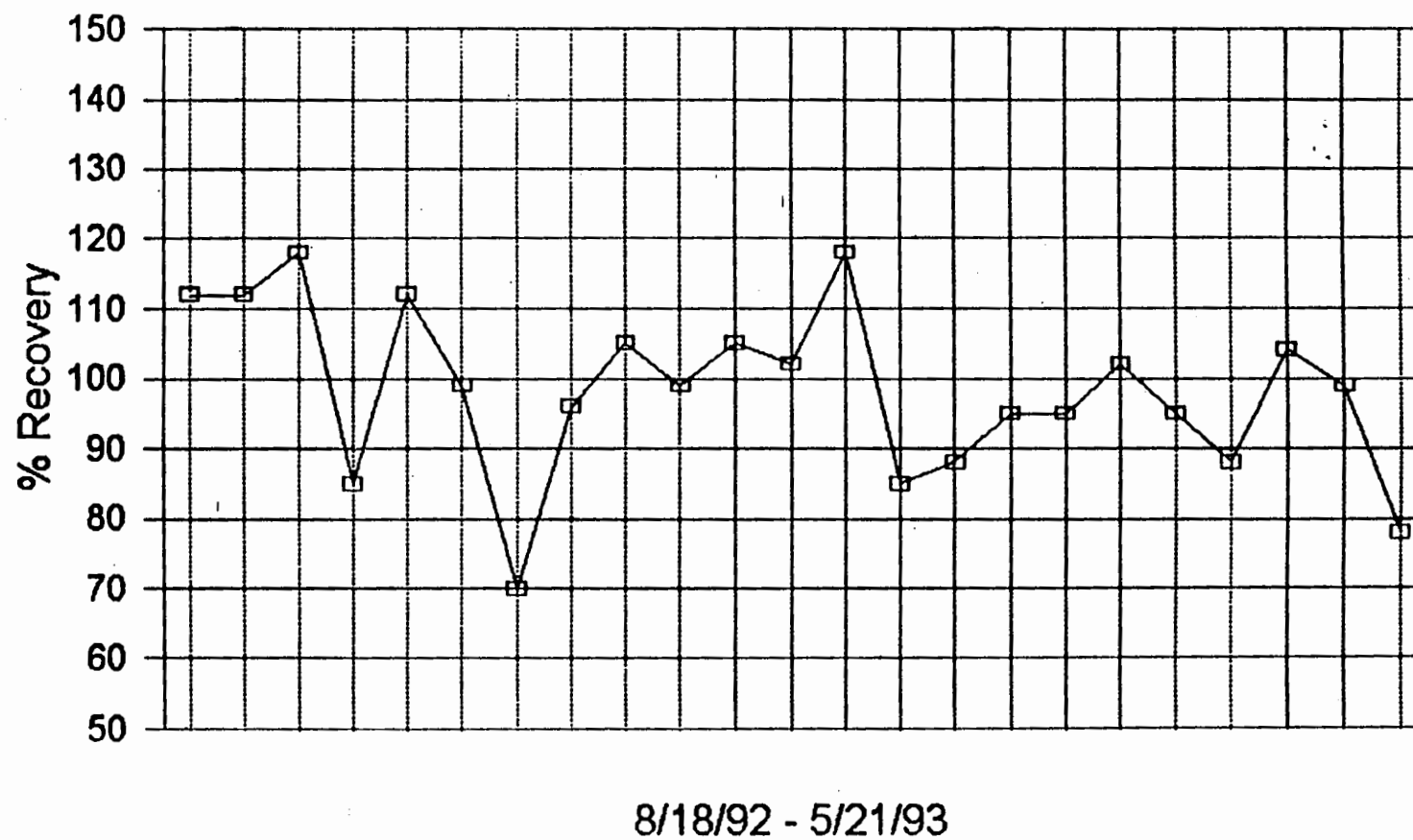
EXAMPLE GC/MS SUMMARY REPORT (HRMS) FOR SAMPLE RUN #32
CALIFORNIA AIR RESOURCES BOARD METHOD 429 POLYCYCLIC AROMATIC HYDROCARBONS

Lab ID: 14129-02 ICAL ID: 12/3/94 16:23:40 Instrument: W
Acquired: 12/3/94 16:23:40 ICAL DATE: 12/3/94 Operator: MPA
Client ID: M429-32 Reviewer: JCM

	RT	RRT	Area	RRF	Amt. (ng)	% REC
Naphthalene	8:21		1.053 E+10	0.67	10,478.37	
2-Methylnaphthalene	9:41		1.790 E+08	1.19	140.98	
Acenaphthylene	11:03		9.371 E+08	1.33	712.59	
Acenaphthene	11:19		7.649 E+06	0.87	8.21	
Fluorene	12:05		2.417 E+07	0.97	30.02	
Phenanthrene	13:17		8.402 E+08	1.10	925.53	
Anthracene	13:21		2.905 E+07	1.02	34.54	
Fluoranthene	14:36		5.932 E+08	1.18	254.36	
Pyrene	14:52		7.611 E+08	1.25	307.62	
Benzo(a)anthracene	16:32		3.120 E+06	1.10	1.9	
Chrysene	16:32		9.620 E+06	1.04	5.2	
Benzo(b)fluoranthene	18:49		1.030 E+06	1.58	7.6	
Benzo(k)fluoranthene	Not found		0.0	1.21		
Benzo(e)pyrene	19:36		1.646 E+07	1.12	13.61	
Benzo(a)pyrene	19:46		4.936 E+06	1.02	3.95	
Perylene	20:01		1.823 E+06	0.64	2.32	
Indeno(1,2,3-c,d)pyrene	23:54		5.728 E+06	2.07	4.37	
Dibenzo(a,h)anthracene	23:56		5.875 E+05	1.66	0.59	
Benzo(g,h,i)perylene	25:09		1.584 E+07	2.11	14.95	
d_8-Naphthalene	8:18	1.000	4.794 E+08	1.16	124.92	62.5
d_8-Acenaphthylene	11:01	1.000	1.972 E+08	1.29	166.07	83.0
d_{10}-Acenaphthene	11:16	1.000	2.142 E+08	1.32	176.19	88.1
d_{10}-Fluorene	12:02	1.000	1.658 E+08	0.94	190.71	95.4
d_{10}-Phenanthrene	13:16	1.000	1.652 E+07	0.81	213.39	106.7
d_{10}-Fluoranthene	14:34	1.000	3.955 E+08	1.03	116.22	58.1
d_{12}-Benzo(a)anthracene	16:28	1.000	2.835 E+08	0.71	121.18	60.6
d_{12}-Chrysene	16:31	1.000	2.987 E+08	0.82	111.08	55.5
d_{12}-Benzo(b)fluoranthene	18:45	1.000	3.439 E+08	1.36	165.79	41.4
d_{12}-Benzo(k)fluoranthene	18:50	1.000	4.304 E+08	2.00	141.02	35.3
d_{12}-Benzo(a)pyrene	19:41	1.000	4.895 E+08	1.96	163.67	40.9
d_{12}-Indeno(1,2,3-c,d)pyrene	23:46	1.000	2.529 E+08	0.92	179.71	44.9
d_{14}-Dibenzo(a,h)anthracene	23:45	1.000	2.400 E+08	0.86	182.65	45.7
d_{12}-Benzo(g,h,i)perylene	24:60	1.000	2.006 E+08	0.78	167.24	41.8
d_{14}-Terphenyl	14:55		7.988 E+08	0.51	523	105
d_{12}-Benzo(e)pyrene	19:32	1.000	3.011 E+08	0.36	676.33	135.3
d_{10}-Anthracene	13:20	1.000	6.795 E+07	0.77	95.29	47.6
d_{10}-2-Methylnaphthalene	9:38	1.000	1.844 E+07	—	100	
d_{10}-Pyrene	14:51	1.000	6.576 E+08	—	100	
d_{12}-Perylene	19:56	1.000	3.057 E+08	—	100	

EXAMPLE LABORATORY REPORT OF PAH RESULTS FOR SAMPLE RUN #32
CALIFORNIA AIR RESOURCES BOARD METHOD 429 POLYCYCLIC AROMATIC HYDROCARBONS

Client ID __M429-32__   Sample Matrix: __M429__   ICAL ID: __ST1120__   Resin Lot #: __LC1130M__
Lab ID: __14129-02__   Date Received: __11/18/94__   ICAL DATE: __12/3/94__   LCS IDs: __14129-LCS1/LCS2__
Instrument: __W____   Date Extracted: __11/30/94__   CONCAL ID: __NA____   LCS DATE: __12/3/94__
Operator: __MPA___   Date Analyzed: __12/3/94__   CONCAL DATE: __NA__
Reviewer: __JCM___   Sample amount: __Sample__   Units: __ng/sample__

COMPOUND:	Conc.	R.L.	Flags
Naphthalene	10478	1600	
2-Methylnaphthalene	141	94	
Acenaphthylene	712	5.0	
Acenaphthene	8.2	5.0	
Fluorene	30	27	
Phenanthrene	930	80	
Anthracene	35	5.0	
Fluoranthene	254	5.0	
Pyrene	307	5.0	
Benzo(a)anthracene	ND	5.0	
Chrysene	6.2	5.0	
Benzo(b)fluoranthene	7.6	5.0	
Benzo(k)fluoranthene	ND	5.0	
Benzo(e)pyrene	14	5.0	
Benzo(a)pyrene	ND	5.0	
Perylene	ND	5.0	
Indeno(1,2,3-c,d)pyrene	ND	5.0	
Dibenzo(a,h)anthracene	ND	5.0	
Benzo(g,h,i)perylene	15	5.0	

Internal Standards (%R)

d_8-Naphthalene	62		
d_8-Acenaphthylene	83		
d_{10}-Acenaphthene	88		
d_{10}-Fluorene	95		
d_{10}-Phenanthrene	107		
d_{10}-Fluoranthene	58		
d_{12}-Benzo(a)anthracene	61		
d_{12}-Chrysene	56		
d_{12}-Benzo(b)fluoranthene	41		H
d_{12}-Benzo(k)fluoranthene	35		H
d_{12}-Benzo(a)pyrene	41		H
d_{12}-Indeno(1,2,3-c,d)pyrene	45		H
d_{14}-Dibenzo(a,h)anthracene	46		H
d_{12}-Benzo(g,h,i)perylene	42		H

Alternate Standard (%R)

d_{10}-Anthracene	48

Surrogate Standard (%R)

d_{14}-Terphenyl	105
d_{12}-Benzo(e)pyrene	135

EXAMPLE OF TESTER'S SUMMARY OF LABORATORY REPORTS

Run #:	31	32	33	Field Blank	Method Blank	LCS #1	LCS #2
	ng/sample					percent recovery	
Naphthalene	4300	10000	460000 *	<1600	<1700	100	103
2-Methylnaphthalene	< 94	140	6400 *	< 94	<78	96	95
Acenaphthylene	140	710	85000 *	9.1	< 5 0	95	97
Acenaphthene	9.2	8.2	500	< 5.0	< 5.0	92	94
Fluorene	27	30	180	< 27	< 27	94	96
Phenanthrene	310	930	43000 *	< 80	< 74	93	94
Anthracene	26	35	2400	5.3	< 5.0	91	89
Fluoranthene	83	250	16000 *	16	< 5.0	90	92
Pyrene	110	310	20000 *	19	< 5.0	87	89
Benzo(a)anthracene	< 5.0	< 5.0	170	< 5.0	< 5.0	87	86
Chrysene	< 5.0	6.2	300	< 5.0	< 5.0	83	89
Benzo(b)fluoranthene	< 5.0	7.6	340	< 5.0	< 5.0	92	93
Benzo(k)fluoranthene	< 5.0	< 5.0	89	< 5.0	< 5.0	92	95
Benzo(e)pyrene	35	< 35	530	6.9	< 5.0	97	99
Benzo(a)pyrene	< 5.0	< 5.0	240	< 5.0	< 5.0	89	92
Perylene	< 5.0	< 5.0	110	< 5.0	< 5.0	89	89
Indeno(1,2,3-c,d)pyrene	< 5.0	< 5.0	100	< 5.0	< 5.0	87	90
Dibenzo(a,h)anthracene	< 5.0	< 5.0	6.4	< 5.0	< 5.0	88	90
Benzo(g,h,i)perylene	< 85	< 85	440	17.0	< 5.0	89	91
Internal Standards (%R)							
d_8-Naphthalene	66	62	57 *	53	55	67	64
d_8-Acenaphthylene	82	83	85 *	73	69	73	70
d_{10}-Acenaphthene	85	88	80 *	81	75	76	75
d_{10}-Fluorene	91	95	102	90	82	79	81
d_{10}-Phenanthrene	106	107	79 *	107	93	88	93
d_{10}-Fluoranthene	79	58	75 *	83	80	84	80
d_{12}-Benzo(a)anthracene	100	61	108	114	93	96	98
d_{12}-Chrysene	91	56	99	102	88	96	91
d_{12}-Benzo(b)fluoranthene	69	41 H	60	85	84	88	85
d_{12}-Benzo(k)fluoranthene	62	35 H	50	78	84	85	84
d_{12}-Benzo(a)pyrene	70	41 H	58	86	89	92	90
d_{12}-Indeno(1,2,3-c,d)pyrene	82	45 H	58	106	106	104	105
d_{14}-Dibenzo(a,h)anthracene	72	42 H	58	92	92	96	96
d_{12}-Benzo(g,h,i)perylene	84	46 H	58	107	104	102	103
Surrogate Standards (%R)							
d_{14}-Terphenyl	125	105	90	123	130		
d_{12}-Benzo(e)pyrene	72	135	112	103	112		
Alternate Standard (%R)							
d_{10}-Anthracene	67	48 H	115	116	101	83	85
Test Date	11/15/94	11/16/94	11/17/94	11/16/94	NA	NA	NA
Date received by lab.	11/18/94	11/18/94	11/18/94	11/18/94	NA	NA	NA
Date extracted	11/30/94	11/30/94	11/30/94	11/30/94	11/30/94	11/30/94	11/30/94
Date analyzed	12/3/94	12/3/94	12/3/94	12/3/94	12/3/94	12/3/94	12/3/94

"<" denotes that the compound was not detected at levels above the indicated reporting limit.

"H" indicates internal Standard Recovery Results below 50%, but signal-to-noise greater than 10:1.

"*" indicates compounds reanalyzed at 1:50 dilution due to saturation.

FIELD DATA SUMMARY FOR PAH EMISSIONS TEST

	RUN ID	31	32	33	
	DATE	11-15-95	11-16-95	11-17-95	
	START/STOP TIME	1015/1435	1020/1645	0855/1525	
	LOCATION	STACK	STACK	STACK	
	STACK DIAMETER	35.5 in.	35.5 in.	35.5 in.	
	NOZZLE DIAMETER	0.3105	0.313 in.	0.3125 in.	
	METER BOX ID	5419	5419	5419	
STANDARD DRY GAS VOLUME	$V_{m(std)}$	145.19	235.57	250.76	DSCF(68° F)
	V_m	132.65	213.67	228.10	cubic ft
	P_{bar}	29.78	29.98	29.88	inches Hg
	ΔH_{avg}	1.15	1.35	1.56	inches H_2O
	T_m	60.0	60.0	60.0	° F
	K_1	17.64	17.64	17.64	
	Y	1.08	1.08	1.08	
PERCENT MOISTURE	B_{ws}	12.9	15.0	18.4	percent
	Impinger + tare	2183.3	2092.3	2063	grams
	Final wt.	2609.8	2934.9	3210.2	grams
	Net imp. catch	426.5	842.6	1147.2	grams
	Silica gel tare	1561.8	1788.8	1585.7	grams
	Post sampling wt.	1590.0	1826.9	1536.2	grams
	Moisture gain	28.2	38.1	49.5	grams
	Total moisture (V_{lc})	454.7	880.7	1196.7	grams
	$V_{w(std)}$	21.43	41.50	56.39	DSCF(68° F)
	$V_{m(std)}$	145.19	235.57	250.76	DSCF(68° F)
	K_2	0.0471	0.0471	0.0471	
MOLECULAR WEIGHT	M_d	29.93	29.95	30.08	lb/lbmole
	M_s	28.40	28.16	27.86	lb/lbmole
	O_2	11.25	10.75	10.00	percent
	CO	0.00	0.00	0.00	percent
	CO_2	9.25	9.50	10.50	percent
	N_2	79.50	79.75	79.50	percent
	B_{ws}	12.86	14.98	18.36	percent
GAS VELOCITY	v_s	38.4	40.88	43.2	feet/second
	Δp	0.530	0.56	0.59	inches H_2O
	T_s	420	428	427	° F
	P_s	-0.27	-0.27	-0.27	inches H_2O
	P_s	29.76	29.96	29.86	inches Hg
	M_s	28.40	28.16	27.86	lb/lbmole
	K_p	85.49	85.49	85.49	
	C_p	0.83	0.83	0.83	
VOLUMETRIC FLOW RATE	Q_{std}	8241	8531	8641	DSCF(68° F)
	B_{ws}	12.86	14.98	18.36	percent
	v_s	38.38	40.88	43.23	feet/second
	A	6.8736	6.8736	6.8736	sq. feet
	sec/min	60	60	60	
	K_1	17.64	17.64	17.64	
ISOKINETIC RATIO	I	96	99	104	percent
	T_s	420	428	427	° F
	$V_{m(std)}$	145.19	235.57	250.76	DSCFM(68° F)
	P_s	29.76	29.96	29.86	inches Hg
	v_s	38.38	40.88	43.23	feet/second
	θ	240	360	360	minutes
	B_{ws}	12.86	14.98	18.36	percent
	A_n	0.00053	0.00053	0.00053	sq. feet
	K_4	0.09450	0.09450	0.09450	

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FIGURE 17C

EXAMPLE OF EMISSIONS TEST REPORT

	Run #31	Run #32	Run #33
(ng/dscm)			
Naphthalene	1046	1499	64782
2-Methylnaphthalene	<23	21.0	901
Acenaphthylene	34	106	11971
Acenaphthene	2.2	1.2	70
Fluorene	6.6	4.5	25
Phenanthrene	75	139	6056
Anthracene	<6.3	5.3	338
Fluoranthene	20	38	2253
Pyrene	27	47	2817
Benzo(a)anthracene	<1.2	<0.75	24
Chrysene	<1.2	0.92	42
Benzo(b)fluoranthene	<1.2	1.1	48
Benzo(k)fluoranthene	<1.2	<0.75	13
Benzo(e)pyrene	<8.5	<5.3	75
Benzo(a)pyrene	<1.2	<0.75	34
Perylene	<1.2	<0.75	16
Indeno(1,2,3-c,d)pyrene	<1.2	<0.75	14
Dibenzo(a,h)anthracene	<1.2	<0.75	0.90
Benzo(g,h,i)perylene	<21	<13	62
(ng/sec)			
Naphthalene	4068	6036	264180
2-Methylnaphthalene	<89	85	3676
Acenaphthylene	132	429	48816
Acenaphthene	8.7	5.0	287
Fluorene	26	18	103
Phenanthrene	293	561	24695
Anthracene	<25	21	1378
Fluoranthene	79	151	9189
Pyrene	104	187	11486
Benzo(a)anthracene	<4.7	<3.0	99
Chrysene	<4.7	3.7	172
Benzo(b)fluoranthene	<4.7	4.6	195
Benzo(k)fluoranthene	<4.7	<3.0	51
Benzo(e)pyrene	<33	<21	304
Benzo(a)pyrene	<4.7	<3.0	138
Perylene	<4.7	<3.0	63
Indeno(1,2,3-c,d)pyrene	<4.7	<3.0	57
Dibenzo(a,h)anthracene	<4.7	<3.0	3.7
Benzo(g,h,i)perylene	<80	<51	253

Standard Conditions: 68 deg.F (20 deg.C) & 29.92 in. Hg. (760 mm Hg)
"<" indicates that the compound was not detected above the reporting limit.

METHOD 429 - APPENDIX A

DETERMINATION OF THE METHOD DETECTION LIMIT

This procedure is based on the approach adopted by the EPA and included as Appendix B to Title 40, Part 136 of the Code of Federal Regulations (40 CFR 136). The samples shall be subjected to the same extraction, concentration, cleanup, and analytical procedures as those required for the field samples.

A1   Procedure

A1.1   Make an estimate of the detection limit (MDL) of each target compound using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise ratio in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent methylene chloride.

(c) That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

(d) Instrumental limitations.

(e) The concentration equivalent to five times the theoretical quantitation limit (Section 8.3.1 of the test method)

The experience of the analyst is important to this process, but one of the above considerations must be included in the initial estimate of the detection limit.

A1.2   Prepare according to the procedures described in Sections 4.2.2.1 to 4.2.2.4 enough XAD-2 resin to provide, at a minimum, eight aliquots each with mass equal to that required to pack a Method 429 sorbent cartridge. A contamination check must be conducted to identify those PAH for which a MDL cannot be determined by this method.

A1.3   To each of seven (7) aliquots of the clean resin, add an amount of each target analyte equal to the estimated detection limit. The mass of each resin aliquot must be known, and should be approximately 40 grams, the amount required to pack a Method 429 sorbent cartridge. The eighth aliquot shall be a blank.

A1.4   Process each of the eight samples through the entire PAH analytical method. All quality criteria requirements of the analytical method must be satisfied.

A1.5   Report the analytical results. The laboratory report must satisfy all of the reporting requirements of Section 10 of the test method.

A1.6   It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with step A1.3. This will: (1) prevent repeating this entire procedure and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure a good estimate of the method detection, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in step A1.3. Evaluate these data:

(1) If the sample levels are in a desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL according to Section A2.

(2) If these measurements indicate the selected analyte level is not in correct range, re-estimate the MDL with a new sample as in A1.2 and repeat steps A1.3 to A1.5.

A2   CALCULATION

A2.1   Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1} \left[\sum_{i=1}^{n} x_i^2 - \frac{\left(\sum_{i=1}^{n} x_i^2 \right)}{n} \right]$$

429-(A)-(1)

$$S = \sqrt[2]{S^2}$$

Where:

X_i, i = 1 to n, are the analytical results in the final method reporting units obtained from the n sample aliquots and Σ refers to the sum of the X values from i = 1 to n.

A2.2   (a) Compute the MDL as follows:

$$MDL = t_{(n-1,\ 1-\alpha\ =\ 0.99)} \times (S)$$

429(A)-(2)

Where:

MDL = the method detection limit

$t_{(n-1,\ 1-\alpha\ =\ 0.99)}$ = Students' t-value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. See Table 429(A)-1.

S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in A2.2(a) are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (χ^2/df).

$$LCL = 0.64\ MDL$$
$$UCL = 2.20\ MDL$$

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

A3   OPTIONAL ITERATIVE PROCEDURE

A3.1   This is to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step A1.1, take the MDL as calculated in Step A2.2, spike the matrix at this calculated MDL and repeat the procedure starting with Step A1.3.

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger S^2 into the numerator S^2_A and the other into the denominator S^2_B. The computed F-ratio is then compared with

the F-ratio found in the table which is 3.05 as follows: if $S^2_A/S^2_B < 3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S^2_A + 6S^2_B}{12} \right] \qquad 429(A)\text{-}(3)$$

if $S^2_A/S^2_B > 3.05$, respike at the most recent calculated MDL and process the samples through the procedure starting with Step A1.3. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S_{pooled} as calculated in Equation 429(A)-3 to compute the final MDL according to the following equation:

$$MDL = 2.681(S_{pooled})$$
                                           429(A)-(4)

Where: 2.681 is equal to $t_{(12, 1-\alpha = .99)}$.

(d) The 95% confidence limits for MDL calculated using Equation 429(A)-4 are computed according to the following equations derived from percentiles of the chi squared over degrees of freedom distribution.

LCL = 0.72 MDL
UCL = 1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

TABLE 429(A)-1

SELECTED STUDENT'S t VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of Replicates	Degrees of Freedom (n-1)	$t_{(n-1, .99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390

N-4
Chlorine Protocol

i. Thioacetamide solution: Dissolve 250 mg CH₃CSNH₂ in 100 mL distilled water. (CAUTION: *Cancer suspect agent. Take care to avoid skin contact or ingestion.*)

j. Chlorine-demand-free water: See C.3m.

k. Glycine solution: Dissolve 20 g glycine (aminoacetic acid) in sufficient chlorine-demand-free water to bring to 100 mL total volume. Store under refrigerated conditions and discard if cloudiness develops.

l. Barium chloride crystals, BaCl₂·2H₂O.

3. Procedure

The quantities given below are suitable for concentrations of total chlorine up to 5 mg/L. If total chlorine exceeds 5 mg/L, use a smaller sample and dilute to a total volume of 100 mL. Mix usual volumes of buffer reagent and DPD indicator solution, or usual amount of DPD powder, with distilled water *before* adding sufficient sample to bring total volume to 100 mL. (If sample is added before buffer, test does not work.)

If chromate is present (>2 mg/L) add and mix 0.2 g BaCl₂·2H₂O/ 100 mL sample before adding other reagents. If, in addition, sulfate is >500 mg/L, use 0.4 g BaCl₂·2H₂O/100 mL sample.

a. Free chlorine or chloramine: Place 5 mL each of buffer reagent and DPD indicator solution in titration flask and mix (or use about 500 mg DPD powder). Add 100 mL sample, or diluted sample, and mix.

1) Free chlorine—Titrate rapidly with standard FAS titrant until red color is discharged (Reading *A*).

2) Monochloramine—Add one very small crystal of KI (about 0.5 mg) or 0.1 mL (2 drops) KI solution and mix. Continue titrating until red color is discharged again (Reading *B*).

3) Dichloramine—Add several crystals KI (about 1 g) and mix to dissolve. Let stand for 2 min and continue titrating until red color is discharged (Reading *C*). For dichloramine concentrations greater than 1 mg/L, let stand 2 min more if color driftback indicates slightly incomplete reaction. When dichloramine concentrations are not expected to be high, use half the specified amount of KI.

4) Simplified procedure for free and combined chlorine or total chlorine—Omit 2) above to obtain monochloramine and dichloramine together as combined chlorine. To obtain total chlorine in one reading, add full amount of KI at the start, with the specified amounts of buffer reagent and DPD indicator, and titrate after 2 min standing.

b. Nitrogen trichloride: Place one very small crystal of KI (about 0.5 mg) or 0.1 mL KI solution in a titration flask. Add 100 mL sample and mix. Add contents to a second flask containing 5 mL each of buffer reagent and DPD indicator solution (or add about 500 mg DPD powder direct to the first flask). Titrate rapidly with standard FAS titrant until red color is discharged (Reading *N*).

c. Free chlorine in presence of bromine or iodine: Determine free chlorine as in ¶ 3a1). To a second 100-mL sample, add 1

mL glycine solution before adding DPD and buffer. Titrate according to ¶ 3a1). Subtract the second reading from the first to obtain Reading A.

4. Calculation

For a 100-mL sample, 1.00 mL standard FAS titrant = 1.00 mg Cl as Cl₂/L.

Reading	NCl₃ Absent	NCl₃ Present
A	Free Cl	Free Cl
B − A	NH₂Cl	NH₂Cl
C − B	NHCl₂	NHCl₂ + ½NCl₃
N	—	Free Cl + ½NCl₃
2(*N − A*)	—	NCl₃
C − N	—	NHCl₂

In the event that monochloramine is present with NCl₃, it will be included in *N*, in which case obtain NCl₃ from 2(*N − B*).

Chlorine dioxide, if present, is included in *A* to the extent of one-fifth of its total chlorine content.

In the simplified procedure for free and combined chlorine, only *A* (free Cl) and *C* (total Cl) are required. Obtain combined chlorine from *C − A*.

The result obtained in the simplified total chlorine procedure corresponds to *C*.

5. Precision and Bias

See B.5.

6. Bibliography

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Methods for the Examination of Waters and Associated Materials Chemical Disinfecting Agents in Water and Effluents, and Chlorine Demand. 1980. Her Majesty's Stationery Off., London. England.

4500-Cl G.   DPD Colorimetric Method

1. General Discussion

a. Principle: This is a colorimetric version of the DPD method and is based on the same principles. Instead of titration with

standard ferrous ammonium sulfate (FAS) solution as in the titrimetric method, a colorimetric procedure is used.

b. Interference: See A.3 and F.1d. Compensate for color and turbidity by using sample to zero photometer. Minimize chro-

mate interference by using the thioacetamide blank correction.

c. Minimum detectable concentration: Approximately 10 μg Cl as Cl_2/L. This detection limit is achievable under ideal conditions; normal working detection limits typically are higher. ·

2. Apparatus

a. Photometric equipment: One of the following is required:

1) *Spectrophotometer,* for use at a wavelength of 515 nm and providing a light path of 1 cm or longer.

2) *Filter photometer,* equipped with a filter having maximum transmission in the wavelength range of 490 to 530 nm and providing a light path of 1 cm or longer.

b. Glassware: Use separate glassware, including separate spectrophotometer cells, for free and combined (dichloramine) measurements, to avoid iodide contamination in free chlorine measurement.

3. Reagents

See F.2*a, b, c, d, e, h, i,* and *j.*

4. Procedure

a. Calibration of photometric equipment: Calibrate instrument with chlorine or potassium permanganate solutions.

1) Chlorine solutions—Prepare chlorine standards in the range of 0.05 to 4 mg/L from about 100 mg/L chlorine water standardized as follows: Place 2 mL acetic acid and 10 to 25 mL chlorine-demand-free water in a flask. Add about 1 g KI. Measure into the flask a suitable volume of chlorine solution. In choosing a convenient volume, note that 1 mL $0.025N$ $Na_2S_2O_3$ titrant (see B.2*d*) is equivalent to about 0.9 mg chlorine. Titrate with standardized $0.025N$ $Na_2S_2O_3$ titrant until the yellow iodine color almost disappears. Add 1 to 2 mL starch indicator solution and continue titrating to disappearance of blue color.

Determine the blank by adding identical quantities of acid, KI, and starch indicator to a volume of chlorine-demand-free water corresponding to the sample used for titration. Perform blank titration A or B, whichever applies, according to B.3*d*.

$$mg\ Cl\ as\ Cl_2/mL = \frac{(A + B) \times N \times 35.45}{mL\ sample}$$

where:

N = normality of $Na_2S_2O_3$,
A = mL titrant for sample,
B = mL titrant for blank (to be added or subtracted according to required blank titration. See B.3*d*).

Use chlorine-demand-free water and glassware to prepare these standards. Develop color by first placing 5 mL phosphate buffer solution and 5 mL DPD indicator reagent in flask and then adding 100 mL chlorine standard with thorough mixing as described in *b* and *c* below. Fill photometer or colorimeter cell from flask and read color at 515 nm. Return cell contents to flask and titrate with standard FAS titrant as a check on chlorine concentration.

2) Potassium permanganate solutions—Prepare a stock solution containing 891 mg $KMnO_4$/1000 mL. Dilute 10.00 mL stock solution to 100 mL with distilled water in a volumetric flask. When 1 mL of this solution is diluted to 100 mL with

distilled water, a chlorine equivalent of 1.00 mg/L will be produced in the DPD reaction. Prepare a series of $KMnO_4$ standards covering the chlorine equivalent range of 0.05 to 4 mg/L. Develop color by first placing 5 mL phosphate buffer and 5 mL DPD indicator reagent in flask and adding 100 mL standard with thorough mixing as described in *b* and *c* below. Fill photometer or colorimeter cell from flask and read color at 515 nm. Return cell contents to flask and titrate with FAS titrant as a check on any absorption of permanganate by distilled water.

Obtain all readings by comparison to color standards or the standard curve before use in calculation.

b. Volume of sample: Use a sample volume appropriate to the photometer or colorimeter. The following procedure is based on using 10-mL volumes; adjust reagent quantities proportionately for other sample volumes. Dilute sample with chlorine-demand-free water when total chlorine exceeds 4 mg/L.

c. Free chlorine: Place 0.5 mL each of buffer reagent and DPD indicator reagent in a test tube or photometer cell. Add 10 mL sample and mix. Read color immediately (Reading *A*).

d. Monochloramine: Continue by adding one very small crystal of KI (about 0.1 mg) and mix. If dichloramine concentration is expected to be high, instead of small crystal add 0.1 mL (2 drops) freshly prepared KI solution (0.1 g/100 mL). Read color immediately (Reading *B*).

e. Dichloramine: Continue by adding several crystals of KI (about 0.1 g) and mix to dissolve. Let stand about 2 min and read color (Reading *C*).

f. Nitrogen trichloride: Place a very small crystal of KI (about 0.1 mg) in a clean test tube or photometer cell. Add 10 mL sample and mix. To a second tube or cell add 0.5 mL each of buffer and indicator reagents; mix. Add contents to first tube or cell and mix. Read color immediately (Reading *N*).

g. Chromate correction using thioacetamide: Add 0.5 mL thioacetamide solution (F.2*i*) to 100 mL sample. After mixing, add buffer and DPD reagent. Read color immediately. Add several crystals of KI (about 0.1 g) and mix to dissolve. Let stand about 2 min and read color. Subtract the first reading from Reading *A* and the second reading from Reading *C* and use in calculations.

h. Simplified procedure for total chlorine: Omit Step *d* above to obtain monochloramine and dichloramine together as combined chlorine. To obtain total chlorine in one reading, add the full amount of KI at the start, with the specified amounts of buffer reagent and DPD indicator. Read color after 2 min.

5. Calculation

Reading	NCl_3 Absent	NCl_3 Present
A	Free Cl	Free Cl
B − A	NH_2Cl	NH_2Cl
C − B	$NHCl_2$	$NHCl_2 + \frac{1}{2}NCl_3$
N	—	Free Cl + $\frac{1}{2}NCl_3$
$2(N − A)$	—	NCl_3
C − N	—	$NHCl_2$

In the event that monochloramine is present with NCl_3, it will be included in Reading *N*, in which case obtain NCl_3 from $2(N − B)$.

6. Bibliography

See F.6.

Standard Test Method for
Single Batch Extraction Method for Wastes[1]

This standard is issued under the fixed designation D 5233; 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. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method is applicable to the extraction of samples of treated or untreated solid wastes or sludges, or solidified waste samples, to provide an indication of the leaching potential.

1.2 This test method is intended to provide an extract for measurement of the concentration of the analytes of concern. The measured values may be compared against set or chosen acceptance levels in some applications.

1.3 If the sole application of the test method is such a pass/fail comparison and a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that the chosen acceptance concentration levels could not possibly be exceeded, the test method need not be run.

1.4 If the sole application of the test method is such a pass/fail comparison and an analysis of any one of the liquid fractions of the extract indicates that the concentration of the target analyte is so high that, even after accounting for dilution from the other fractions of the extract, it would be equal to or above an acceptance concentration level, then the waste fails the test. In such a case it may not be necessary to analyze the remaining fractions of the extract.

1.5 This test method is intended to provide an extract suitable for the measurement of the concentration of analytes that will not volatilize under the conditions of the test method.

1.6 Presence of volatile analytes may be established if an analysis of the extract obtained using this test method detects the target volatile analyte. If its concentration is equal to or exceeds an acceptance level for that analyte, the waste fails the test. However, extract from this test method shall not be used to determine the concentration of volatile organic analytes.

1.7 This test method is intended to describe only the procedure for performing a batch extraction. It does not describe all of the sampling and analytical requirements that may be associated with the application of this test method.

1.8 The values stated in either SI or inch-pound units are to be regarded as the standard. The values given in parentheses are for information only.

1.9 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For a specific*

precautionary statement, see Note 8.

2. Referenced Documents

2.1 *ASTM Standards:*

D 75 Practices for Sampling Aggregates[2]

D 420 Practice for Investigating and Sampling Soil and Rock for Engineering Purposes[3]

D 653 Terminology Relating to Soil, Rock, and Contained Fluids[3]

D 1129 Terminology Relating to Water[4]

D 1193 Specification for Reagent Water[4]

D 2234 Test Method for Collection of a Gross Sample of Coal[5]

D 3370 Practices for Sampling Water[4]

E 122 Practice for Choice of Sample Size to Estimate A Measure of Quality for a Lot or Process[6]

ES 16 Practice for the Generation of Environmental Data Related to Waste Management Activities[7]

3. Terminology

3.1 *Definitions*—For definitions of terms used but not defined in this test method, see Terminology D 1129.

4. Summary of Test Method (See Figure 1)

4.1 For wastes containing less than 0.5 % dry solid material, the filtrate of the waste, after filtration through a 0.6 to 0.8-μm glass fiber filter, is defined as the method extract. Extraction of the solid is not required for such wastes.[8,9]

4.2 For wastes containing greater than or equal to 0.5 % dry solid material, the liquid, if any, is separated from the solid phase and stored for later analysis. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid used is a function of the alkalinity of the solid phase of the waste. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8-μm glass fiber filter.

4.3 If compatible (that is, multiple phases will not form upon combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the

[1] This test method is under the jurisdiction of ASTM Committee D-34 on Waste Disposal and is the direct responsibility of Subcommittee D34.02 on Physical and Chemical Characterization.

Current edition approved March 15, 1992. Published May 1992.

[2] *Annual Book of ASTM Standards,* Vol 04.03.
[3] *Annual Book of ASTM Standards,* Vol 04.08.
[4] *Annual Book of ASTM Standards,* Vol 11.01.
[5] *Annual Book of ASTM Standards,* Vol 05.05.
[6] *Annual Book of ASTM Standards,* Vol 14.02.
[7] *Annual Book of ASTM Standards,* Vol 11.04 (see 1991 edition).
[8] *Federal Register,* Vol 55, No. 61, March 29, 1990. Toxicity Characteristics Revisions, Final Rule.
[9] *Federal Register,* Vol 55, No. 126, June 29, 1990. Toxicity Characteristic Revisions, Final Rule, Corrections.

FIG. 1 Method Flow Chart

results are combined mathematically to yield a volume-weighted average concentration.

5. Significance and Use

5.1 This test method is intended to generate an extract with a concentration of the target analyte(s) representative of the expected release under the scenario simulated, and which can be compared with concentration levels acceptable in waste disposal, treatment, or production activities.

5.2 The extraction conditions of the test method were chosen to simulate a potential disposal scenario to which the wastes may be exposed.

5.3 One intent of this test method is that the amount of acid in the extraction fluids reflect the acid available from the leachate of a specific landfill where municipal and industrial wastes were co-disposed.[10]

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[10] Kimmel, T. A., and Friedman, D. A., "Model Assumptions and Rationale behind the Development of EP III," *ASTM STP 886*, J. K. Petros, et al, Eds., ASTM, Philadelphia, PA, 1986, pp. 36–53.

5.4 One intent of this test method is to not allow the pH of the extraction fluid to be lower than that of the leachate of a specific landfill where municipal and industrial wastes were co-disposed. Therefore, the pH of the extraction fluid was chosen with the following considerations:

(1) Not to be less than 4.93 ± 0.05 for the extraction of wastes with an acid neutralization capacity of less than the acid available in the total volume of extraction fluid used in the method (Extraction Fluid No. 1).

(2) At 2.88 ± 0.05, as defined by the pH of the acid, for the extraction of wastes with an acid neutralization capacity of more than the acid available in the extraction fluid used in the method (Extraction Fluid No. 2).

5.5 The interpretation and use of the results of this test method are limited by the assumptions of a single co-disposal scenario and by the factors affecting the composition of a landfill leachate and chemical or other differences between a selected extraction fluid and the real landfill leachate.

5.6 This test method may be affected by biological

FIG. 2 Rotary Agitation Apparatus

changes in the waste, and it is not designed to isolate or measure the effect of such processes.

5.7 This test method produces extracts that are amenable to the determination of both minor and major constituents. When minor constituents are being determined, it is especially important that precautions be taken in sample storage and handling to avoid possible contamination of the samples.

5.8 The agitation technique, rate, liquid-to-solid ratio, and filtration conditions specified in the method may not be suitable for extracting all types of wastes.

5.9 This test method is intended to extract the samples in their original physical state as is, without any size reduction. However, the sample/extractor interaction is expected to correlate with the environmental conditions to which a waste may be exposed.[11]

5.10 The extraction conditions defined by this test method are expected to yield steady-state concentrations, determined by the extraction liquid-to-solid ratio and the duration of the extraction, which may or may not agree with the concentration of an equilibrium.

6. Apparatus and Materials

6.1 *Agitation Apparatus*, capable of rotating the extraction vessel in an end-over-end fashion (see Fig. 2), at 30 ± 2 r/min, such that the axis of rotation is horizontal and passes through the center of the bottle.

NOTE 1—Similar devices may be used having a different axle arrangement if equivalency can be demonstrated.

6.2 *Extraction Vessel*—Suitable vessels include cylindrically shaped, minimum 2-L size, with capacity sufficient to hold the sample and the extraction fluid. Head-space is allowed in this vessel. The extraction bottles may be constructed from various plastic materials, depending on the analytes of interest and the nature of the waste. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated. The bottles should be sturdy, in order to withstand the impact of the falling sample fragments, and shall have a leak-free seal. The use of polytetrafluoroethylene tape is recommended to ensure a tight seal. Due to their potential for breakage, the use of glass bottles is not recommended.

[11] *Federal Register*, Vol 53. No. 100, May 24, 1988. Proposed Cage Modification of TCLP.

NOTE 2—Suitable bottles range from 4.0 to 4.5 in. (102 to 114 mm) in diameter and from 8.5 to 13.0 in. (216 to 330 mm) in height.

6.3 *Filtration Device*—It is recommended that all filtrations be performed in a hood. Wastes should be filtered using positive-pressure filtration using a pre-purified grade inert gas such as nitrogen.

6.3.1 *Filter Holder*, capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation (maximum 50 psi or 345 kPa). These devices shall have a minimum internal volume of 300 mL and shall be equipped to accommodate a minimum filter size of 47 mm. (Filter holders having an internal capacity of 2.2 L and equipped to accommodate a 142-mm diameter filter are recommended.)

6.3.1.1 *Materials of Construction*—Filtration devices shall be made of inert materials that will not leach or adsorb the analytes of concern. Glass, polytetrafluoroethylene, or type 316 stainless steel equipment may be used when both organic and inorganic analytes are of concern. Devices made of high-density polyethylene (HDPE), polypropylene (PP), or polyvinylchloride (PVC) may be used when only inorganics are of concern.

6.4 *Filters*, made of borosilicate glass fiber, containing no binder materials, and having an effective pore size of 0.6 to 0.8 μm. Pre-filters must not be used. When inorganic analytes are of concern, the filter shall be acid washed prior to use by rinsing with 1 N nitric acid followed by three consecutive rinses with Type II reagent water as defined in Specification D 1193. (A minimum of 1 L per rinse is recommended.) Glass fiber filters are fragile and should be handled with care.

6.5 *pH Meter*, with a readability of 0.01 unit and an accuracy of ±0.05 unit at 25°C.

6.6 *Laboratory Balance*, accurate to within ±0.01 g. (All weight measurements are to be within ±0.1 g.)

6.7 *Beakers or Erlenmeyer Flasks*. glass 500-mL, and 2-L.

6.8 *Watch-Glass*, with an appropriate diameter to cover the beaker or Erlenmeyer flask.

6.9 *Magnetic Stirrer*.

6.10 *Mold*, cylindrical, made of inert, non-adsorbing and non-contaminating material for casting of laboratory samples.

6.11 *Straightedge*, made of stainless steel.

6.12 *Impermeable Sheet or Glazed Paper*.

6.13 *Volumetric Flask*, 1-L size.

6.14 *Drying Oven*—Any thermostatically controlled drying oven capable of maintaining a temperature between 85 and 115°C within ±5°C.

6.15 *Graduated Pipet*, readable to 0.1 mL.

6.16 *Hot Plate*, equipped for agitation and temperature control capable of maintaining a 50 ± 3°C temperature.

6.17 *Graduated Measuring Cylinder*, with a precision of ±3 %.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chem-

TABLE 1 Sample Maximum Holding Times, Days

Period Compound	From Field Collection to Method Extraction	From the End of Extraction to the Start of Filtration, h	From Method Extraction to Analytical Extraction	From the Analytical Extraction to the Chemical Analysis	Total Time, Days
Organics	14	2	7	40	61
Mercury	28	2	NA	28	56
Inorganics except Mercury	180	2	NA	180	360

ical Society, where such specifications are available.[12] 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.

7.2 *Purity of Water*—Reagent water is defined as water in which an interfering analyte is not observed at or above the method detection limit of the analyte(s) of interest. Type II of Specification D 1193 or equivalent meets the definition of reagent water.

7.3 *Hydrochloric Acid* (HCl), 1 N, made from ACS reagent grade.

7.4 *Nitric Acid* (HNO₃), 1 N, made from ACS reagent grade.

7.5 *Sodium Hydroxide* (NaOH), 1 N, made from ACS reagent grade.

7.6 *Glacial Acetic Acid* (CH₃COOH), ACS reagent grade.

7.7 *Extraction Fluids*—Several batches or multiple volumes of extraction fluids should be prepared in accordance with the number of extractions. The volume needed for an individual extraction is approximately 2 L. The extraction fluids should be monitored frequently for impurities. The pH should be examined prior to extraction to ensure that these fluids were made up accurately. If impurities are found or the pH is not within the specifications, the fluid shall be discarded and fresh extraction fluid prepared.

7.7.1 *Extraction Fluid* No. 1—Add 5.7 mL glacial acetic acid to 500 mL of reagent water, add 64.3 mL of 1 N NaOH, and dilute to a volume of 1 L. When correctly prepared, the pH of this fluid will be 4.93 ± 0.05.

7.7.2 *Extraction Fluid* No. 2—Dilute 5.7 mL glacial acetic acid with reagent water to a volume of 1 L. When correctly prepared, the pH of this fluid will be 2.88 ± 0.05.

8. Sampling

8.1 If representative samples of the waste must be tested, use ASTM Sampling methods developed for the specific industry where available (see Practices D 75, D 420, D 3370, Terminology D 653, and Method D 2234).

8.2 All samples shall be collected using an appropriate sampling plan to ensure sample integrity and representativeness (see Practice E 122).

8.3 Where no specific methods are available, sampling methodology for materials of similar physical form shall be used.

8.4 It is important that the sample of the waste be representative with respect to surface area, as variations in surface area would directly affect the extraction characteristics of the sample. Waste samples should contain a representative distribution of particle sizes.

NOTE 3—Information on obtaining representative samples can also be found in *Pierre Gy's Sampling Theory and Practice*.[13]

8.5 Approximately 100 g of solid phase samples are required for each extraction. Preliminary evaluation also requires 100 g of solid phase sample. A larger sample size may be required, depending on the solids content of the waste sample (percent solids; see 10.2.9).

8.6 Enough extract should be generated such that the volume will be sufficient to support all of the analyses required. If the volume of extract generated by the performance of a single extraction will not be sufficient to perform all of the analyses to be conducted, it is recommended that more than one extraction be performed and that the extracts from each extraction be combined and then aliquoted for analysis.

8.7 For the evaluation of solidified or stabilized wastes, or both, samples may be cast in the form of a cylinder that will fit into the extraction apparatus. Such cylinders may be used for the evaluation. The casting may be allowed to cure for 30 days before the extraction procedure is performed. For other monolithic materials, a coring may be produced that will fit into the extraction apparatus. Waste materials to which these casting and coring procedures apply include concrete materials, rock, wood, slag, and so forth.

8.8 Quality control measures may require additional samples.

9. Sample Handling and Preparation

9.1 For free-flowing particulate solid wastes, obtain a sample in accordance with the requirements of Section 8 by quartering the sample received for testing on an impermeable sheet of glazed paper, or other flexible non-contaminating material, as follows:

9.1.1 Empty the sample container into the center of the sheet.

9.1.2 Flatten out the sample gently with a suitable straightedge until it is spread uniformly to a depth at least twice the maximum particle diameter.

9.1.3 Remix the sample by lifting a corner of the sheet and drawing low across to the opposite corner in the manner that the material is made to roll over and over and does not merely slide along. Return that corner to its original position. Continue the operation with each corner, proceeding in a clockwise direction. Repeat this cycle ten times.

9.1.4 Lift all four corners of the sheet toward the center, and holding all four corners together, raise the entire sheet into the air to form a pocket for the sample.

[12] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. 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, NY, and the "United States Pharmacopeia."

[13] Pitard, F., *Pierre Gy's Sampling Theory and Practice*. Volumes I and II, CRC Press, 1989.

9.1.5 Repeat 9.1.2.

9.1.6 Gently divide the sample into quarters with a straightedge, one at least as long as the flattened mound of sample. Make an effort to avoid using pressure on the straightedge sufficient to cause damage to the particles.

9.1.7 Discard alternate quarters.

9.1.8 If further reduction of the sample volume is necessary, repeat 9.1.3 through 9.1.7. Use a sample volume to give 100 g of solid for each extraction. Provide additional samples for the preliminary evaluation.

9.2 For field-cored solid wastes or castings produced in the laboratory, cut a representative section weighing approximately 100 g for each extraction plus the preliminary evaluation. Take samples for the preliminary evaluation at the same time as the test samples.

9.2.1 If necessary, shape the sample so that its largest dimension would not exceed the radius of the extraction bottle. (The material shall move freely while fully covered with the extraction fluid.)

9.3 Preservatives shall not be added to the samples prior to extraction.

9.4 For multi-phasic wastes, mix thoroughly to ensure that a representative sample will be withdrawn.

9.5 Samples shall be stored at 4°C to minimize changes due to biological processes. If precipitation occurs, the entire sample (including precipitate) of the precipitate existing at room temperature (see 4.1 and 4.2) should be used.

9.6 The method filtrates and extracts should be prepared for analysis and analyzed as soon as possible. Filtrates and extracts or their portions for metallic analyte determinations should be acidified with nitric acid to pH <2 unless precipitation occurs. To minimize losses, filtrates or extracts or their portions for organic contaminant determinations shall not be allowed to make contact with the atmosphere (that is, head-space).

9.7 Sample maximum holding times (days) are given in Table 1.

10. Preliminary Evaluations and Pre-Extraction Procedures

10.1 Perform preliminary method evaluations on a minimum 100-g aliquot of waste. This aliquot may not undergo the actual extraction. These preliminary evaluations include the determination of the following: (1) percent solids, (2) whether the waste contains dry solids in excess of 0.5 %, and (3) which of the two extraction fluids are to be used for extraction of the waste.

10.2 *Preliminary Determination of Percent Solids*—Percent solids is defined as that fraction of the waste sample (as a percent of the total sample w/w) from which no liquid may be forced out by an applied pressure as described below.

10.2.1 If the waste will obviously yield no free liquid when subjected to pressure filtration of this method (that is, 100 % solids), proceed to 10.4.

NOTE 4—Some materials may look like dry solids but may release liquids under pressure, for example, adsorbents, filter cakes, paint, and other sludges. If uncertain, proceed to the filtration step (10.2.2).

10.2.2 If the sample is liquid or multi-phasic, liquid/solid separation to make a preliminary evaluation of percent solids is required. This involves the filtration device described in 6.3, and the procedure is outlined in 10.2.3 through 10.2.9.

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

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

10.2.5 Weigh out a sub-sample of the waste (100-g minimum) and record the weight.

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

10.2.7 Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). Spread the waste sample evenly over the surface of the filter. Allow the sample to warm to room temperature in the device before filtering.

NOTE 5—If some waste material (>1 % of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in 10.2.5 to determine the weight of the waste sample that will be filtered.

10.2.7.1 Gradually apply gentle pressure of 1 to 10 psi (7 to 70 kPa), until the pressurizing gas moves through the filter. If this point is not reached below 10 psi (69 kPa), and if no additional liquid has passed through the filter in any 2-min interval, slowly increase the pressure in 10-psi (69-kPa) increments to a maximum of 50 psi (345 kPa). After each incremental increase of 10 psi (69 kPa), if the pressurizing gas has not moved through the filter, and if no additional liquid has passed the filter in any 2-min interval, proceed to the next 10-psi (69-kPa) increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (345 kPa) (that is, filtration does not result in any additional filtrate within any 2-min period), stop the filtration.

NOTE 6—Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

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

NOTE 7—Some wastes, such as oily and some paint wastes, will obviously contain some material that appears to be liquid. Even after applying the pressure filtration as outlined in 10.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as solid. Do not replace the original filter under any circumstances. Use only one filter.

10.2.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see 10.2.3) from the total weight of the container plus filtrate. Determine the weight of the solid phase of the waste sample by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in 10.2.5 or 10.2.7. Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{percent solids} = \frac{\text{weight of solid (10.2.9)}}{\text{total weight of waste (10.2.5 or 10.2.7)}} \times 100 \quad (1)$$

10.3 If the percent solids determined in 10.2.9 is equal to or greater than 0.5 %, proceed with the filtered solid phase to

10.3.1. If the percent solids determined in 10.2.9 is less than 0.5 %, the initial liquid phase becomes the method extract. Measure the pH and proceed with this method extract to 11.16.

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

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

NOTE 8: Caution—Take care to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or another appropriate device.

10.3.3 Calculate the percent dry solids as follows:

percent dry solids

$$= \frac{(\text{weight of dry waste} + \text{filter}) - \text{tared weight of filter}}{\text{initial weight of waste (10.2.5 or 10.2.7)}} \quad (2)$$

10.3.4 If the percent dry solids is less than 0.5 %, the initial liquid phase becomes the method extract. Proceed with the extract to 11.16. Measure the pH of the method extract. If the percent dry solids is greater than or equal to 0.5 %, return to the beginning of this section and filter a small, fresh portion of the waste to determine the appropriate extraction fluid (10.4). Since the original sample was destroyed by drying and the preliminary evaluation has been completed, proceed to 11.3 to perform the extraction procedure on a fresh sample.

10.4 *Determination of Appropriate Extraction Fluid* (See Fig. 3)—If the dry solids content of the waste is greater than or equal to 0.5 %, perform the determination of the appropriate fluid (7.7) to be used for the extraction as follows:

10.4.1 Weigh out a small sub-sample of the solid phase of the waste; reduce the solid, if necessary, to a fragment size of approximately 1 mm in diameter or less; and transfer 5.0 g of the solid phase of the waste to a 500-mL beaker or an Erlenmeyer flask.

10.4.2 Add 96.5 mL of reagent water to the beaker, cover with a watch-glass, and stir vigorously for 5 min using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use Extraction Fluid No. 1. Proceed to Section 11.

10.4.3 If the pH from 10.4.2 is >5.0, add 3.5 mL 1 N HCl, slurry briefly, cover with a watch-glass, heat to 50°C, and hold at 50°C for 10 min.

10.4.4 Let the solution cool to room temperature and record the pH. If the pH is <5.0, use Extraction Fluid No. 1. If the pH is >5.0, use Extraction Fluid No. 2. Proceed to Section 11.

10.5 If the aliquot of the waste used for the preliminary evaluation (10.2 through 10.4) was determined to be 100 % solids in 10.2.1, it can be used for Section 11 extraction (assuming that at least 100 g remains). The aliquot subjected to the procedure in 10.2.7 might be appropriate for use in Section 11 if an adequate amount of solids (as determined by 10.2.9) was obtained. The amount of solids necessary is also dependent on whether a sufficient amount of extract will be produced to support the analyses for the target analytes. If an adequate amount of solids remains, proceed to 11.11.
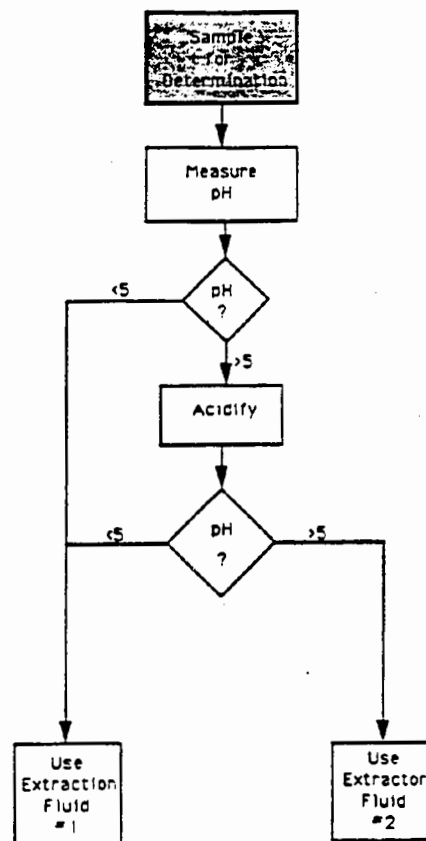
FIG. 3 Determination of the Extraction Fluid

11. Extraction

11.1 A sample size of minimally 100 g (solid and liquid phases) is required. A larger sample size may be appropriate in some cases, depending on the solid contents of the waste sample (percent solids; see 10.2); whether the initial liquid phase (filtrate) will be miscible with the aqueous extract of the solid; and whether inorganics, semivolatile organics, pesticides and herbicides are all analytes of concern. If the amount of extract generated by a single extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

11.2 If the waste will obviously yield no liquid when subjected to pressure filtration (that is, is 100 % solid; 10.2), weigh out a sub-sample of the waste (100 g minimum) and proceed to 11.10.

11.3 If the sample is liquid-like or multi-phasic, liquid-solid separation is required. This involves the filtration device described in 6.3 and is outlined in 11.4 through 11.9.

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

11.5 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if inorganics are of concern (see 6.4).

NOTE 9—Acid washed filters may be used for all extractions, even when inorganics are not of concern.

11.6 Weigh out a sub-sample of waste (100-g minimum) and record the weight. If the waste contains <0.5 % dry solids (10.3), the liquid portion of the waste, after filtration, is defined as the method extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required. For wastes containing >0.5 % dry solids (10.2 or 10.3), use the percent solids information obtained in 10.2 to determine the optimum sample size (100-g minimum) for filtration. Sufficient solid should be generated by filtration to support the analyses to be performed on the method extract.

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

11.8 Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder. Spread the waste sample evenly over the surface of the filter. Allow the sample to warm to room temperature in the device before filtering.

NOTE 10—If some waste material (>1 % of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in 10.2.5 to determine the weight of the waste sample that will be filtered.

11.8.1 Gradually apply gentle pressure of 1 to 10 psi (7 to 70 kPa), until the pressurizing gas moves through the filter. If this point is not reached below 10 psi (69 kPa), and if no additional liquid has passed through the filter in any 2-min interval, slowly increase the pressure in 10-psi (69-kPa) increments to a maximum of 50 psi (345 kPa). After each incremental increase of 10 psi (69 kPa), if the pressurizing gas has not moved through the filter, and if no additional liquid has passed the filter in any 2-min interval, proceed to the next 10-psi (69-kPa) increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (345 kPa) (that is, filtration does not result in any additional filtrate within any 2-min period), stop the filtration.

NOTE 11—Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

11.9 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Measure the pH of the filtrate. Measure the volume of the filtrate (V_1) if the data are to be combined mathematically. Use a graduated measuring cylinder for the volume measurement. The liquid phase may now be analyzed (see 11.13) or stored at 4°C until the time of analysis.

NOTE 12—Some wastes, such as oily and some paint wastes, will obviously contain some material that appears to be liquid. Even after applying the pressure filtration as outlined in 10.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as solid. Do not replace the original filter under any circumstances. Use only one filter.

11.10 If the waste contains <0.5 % dry solids (see 10.3), proceed to 11.14. If the waste contains >0.5 % solids (see 10.2 or 10.3), proceed to 11.11.

11.11 Quantitatively transfer the solid residue retained by the filter, or the solid sample if it did not require filtration, into an extractor bottle. Include the filter if it was used to separate the initial liquid from the solid phase.

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

weight of extraction fluid

$$= \frac{20 \times \text{percent solids (10.2.9)}}{100} \times \text{weight} \dots \quad (3)$$

Slowly add this amount of appropriate extraction fluid (see 10.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that polytetrafluoroethylene tape be used to ensure a tight seal), secure in a rotary agitation device, and rotate at 30 ± 2 r/min for 18 ± 2 h. Ambient temperature (that is, temperature of the room in which the extraction takes place) shall be maintained at 23 ± 2°C during the extraction period.

NOTE 13—As agitation continues, pressure may build up within the extractor bottle for some types of wastes (for example, limed or calcium carbonate-containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be taken under a hood and opened carefully from time to time (for example, after 15 min, 30 min, and 1 h).

11.13 Within 2 h, following the 18 ± 2 h extraction, initiate the separation of the material in the extraction vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in 11.8. For final filtration of the method extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed (see 6.4) if inorganics are of concern.

11.14 Prepare the method extract as follows:

11.14.1 If the waste contained no initial liquid phase, the filtered liquid material obtained from 11.13 is defined as the method extract. Proceed to 11.15.

11.14.2 If compatible (for example, multi-phase waste will not result upon combination), combine the filtered liquid resulting from 11.13 with the initial liquid phase of the waste obtained in 11.8. This combined liquid is defined as the method extract. Proceed to 11.15.

11.14.3 If the initial liquid phase of the waste, as obtained from 11.8, is not or may not be compatible with the filtered liquid resulting from 11.13, do not combine these liquids. Analyze these liquids, collectively defined as the method extract, and combine the results mathematically, as described in 11.15.

11.15 Following collection of the method extract, the pH of the extract should be recorded. The volume of the extract (V_2) shall be measured if the data are to be combined mathematically. Use a graduated measuring cylinder for volume measurement. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with 1 N nitric acid to pH <2. If precipitation is observed upon the addition of nitric acid to a small aliquot of the extract, the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4°C) until analyzed. The method extract shall be prepared and analyzed according to appropriate analytical methods. The method extracts to be analyzed for metals shall be acid-digested except in those instances in which digestion causes a loss of metallic contaminants. If an analysis of the undigested extract reveals that the concentration of any

regulated metallic contaminant exceeds the acceptance level, the waste fails the test and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste met the set acceptance level. If the individual phases are to be analyzed separately, determine the volumes of the individual phases (to ±3 %), using a separatory funnel and graduated cylinder. Conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{final analyte concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2} \quad (4)$$

where:
V_1 = volume of the initial phase (filtrate, L),
C_1 = concentration of the contaminant of concern in the initial phase (mg/L),
V_2 = volume of the extract (L), and
C_2 = concentration of the analyte of concern in the extract (mg/L).

NOTE 14—If either V_1 or V_2 were not detected, use the appropriate detection limit in the calculation.

11.16 Compare the analyte concentration of the method extract with the applicable comparative values. Refer to Section 13 for quality assurance requirements.

12. Report

12.1 Report the following information:

12.1.1 All pH values for the method extract(s);

12.1.2 The concentration of all analytes of concern as measured or calculated in 11.6 and 11.15, respectively;

12.1.3 The type of the extraction fluid used;

12.1.4 The solids content of the sample; and

12.1.5 The dry solids content of the sample if the solids content is >0.5 %.

13. Quality Assurance Requirements

13.1 Maintain all data, including quality assurance data, and keep them available for reference or inspection.

13.2 All quality control measures described in the appropriate analytical methods shall be followed. If the analytical quality control requirements are not specified in the appropriate method, follow the requirements in 13.3 and 13.4 and refer to Practice ES 16.

13.3 A minimum of one blank (using the same extraction fluid and equipment as used for the samples) for every ten extractions that have been conducted shall be used as a check to determine whether any memory effects from the extraction equipment are occurring.

13.4 A matrix spike shall be performed for each waste type where the compositions of the waste matrices are significantly different.

TABLE 2 Precision Data

	High Strength	Low Strength
Mean, %	21.0	1.9
Standard deviation, %	3.0	0.63

NOTE 15—It is recommended that it be assumed that each sample has a significantly different composition unless previous data would indicate otherwise (for example, regular sampling of steady-state process streams). If more than 20 samples of the same waste are being tested, a matrix spike must be performed for every 20 samples.

13.4.1 The matrix spikes are to be added after filtration and combination, if necessary, of the method extract and before preservation.

13.4.2 Matrix spike levels should be established at the appropriate acceptance levels. If the analyte concentration in the method extract is less than one half of the acceptance level, the spike level may be as low as one-half the analyte concentration. However, it shall not be less than the quantitation limit or one-fifth of the acceptance level. In order to avoid differences in the matrix effects, the matrix spikes must be added to the same nominal volume of the method extract as that which was analyzed for the unspiked sample.

13.4.3 The purpose of the matrix spike is to monitor the performance of the analytical method used and to determine whether matrix interference exists. The use of other internal calibration methods, modifications of the analytical methods, or the use of alternate analytical methods may be needed to measure accurately the analyte concentration of the method extract when recovery of matrix spike is below the expected analytical method performance.

13.4.4 Acceptable sample holding times are outlined in 9.7. Exceeding the holding time is not acceptable to establish any compliance with the acceptance levels, but it may be used if the samples are not in compliance.

14. Precision and Bias

14.1 *Precision*—The precision of the procedure in Test Method D 5233 for measuring the sample disintegration, surface area increase, has been evaluated. The fractions retained on 9.5 mm sieve were measured in three laboratories. In each laboratory, duplicate, monolithic samples not passing a 9.5 mm sieve of four high strength and four low strength materials were extracted (see Table 2). The weight of the residual 9.5-mm size fractions was measured and expressed as a percent of the initial sample weight.

14.2 *Bias*—The procedure in Test Method D 5233 for measuring extract generation has no bias because the value of extract is defined only in terms of this method.

15. Keywords

15.1 batch; extraction; laboratory; leaching; single; sludge; solid; solidified; testing; waste

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Percent Solids

the sample. Refrigerate sample at 4°C up to the time of analysis to minimize microbiological decomposition of solids. Preferably do not hold samples more than 24 h. In no case hold sample more than 7 d. Bring samples to room temperature before analysis.

4. Selection of Method

Methods B through F are suitable for the determination of solids in potable, surface, and saline waters, as well as domestic and industrial wastewaters in the range up to 20 000 mg/L.

Method G is suitable for the determination of solids in sediments, as well as solid and semisolid materials produced during water and wastewater treatment.

5. Bibliography

THERIAULT, E.J. & H.H. WAGENHALS. 1923. Studies of representative sewage plants. *Pub. Health Bull.* No. 132.
U.S. ENVIRONMENTAL PROTECTION AGENCY. 1979. Methods for Chemical Analysis of Water and Wastes. Publ. 600/4-79-020, rev. Mar. 1983. Environmental Monitoring and Support Lab., U.S. Environmental Protection Agency, Cincinnati, Ohio.

2540 B.   Total Solids Dried at 103–105°C

1. General Discussion

a. Principle: A well-mixed sample is evaporated in a weighed dish and dried to constant weight in an oven at 103 to 105°C. The increase in weight over that of the empty dish represents the total solids. The results may not represent the weight of actual dissolved and suspended solids in wastewater samples (see above).

b. Interferences: Highly mineralized water with a significant concentration of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing. Exclude large, floating particles or submerged agglomerates of nonhomogeneous materials from the sample if it is determined that their inclusion is not desired in the final result. Disperse visible floating oil and grease with a blender before withdrawing a sample portion for analysis. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue (see 2540A.2).

2. Apparatus

a. Evaporating dishes: Dishes of 100-mL capacity made of one of the following materials:
1) Porcelain, 90-mm diam.
2) Platinum—Generally satisfactory for all purposes.
3) High-silica glass.*
b. Muffle furnace for operation at 550°C.
c. Steam bath.
d. Desiccator, provided with a desiccant containing a color indicator of moisture concentration or an instrumental indicator.
e. Drying oven, for operation at 103 to 105°C.
f. Analytical balance, capable of weighing to 0.1 mg.
g. Magnetic stirrer with TFE stirring bar.
h. Wide-bore pipets.†

3. Procedure

a. Preparation of evaporating dish: If volatile solids are to be measured ignite clean evaporating dish at 550°C for 1 h in a muffle furnace. If only total solids are to be measured, heat clean dish to 103 to 105°C for 1 h. Store and cool dish in desiccator until needed. Weigh immediately before use.

b. Sample analysis: Choose a sample volume that will yield a residue between 10 and 200 mg. When very low total solids are encountered (less than 10 mg/L), less residue may be collected; compensate by using a high-sensitivity balance (0.002 mg). Pipet a measured volume of well-mixed sample to a preweighed dish and evaporate to dryness on a steam bath or in a drying oven. Stir sample with a magnetic stirrer during transfer. If necessary, add successive sample portions to the same dish after evaporation. When evaporating in a drying oven, lower temperature to approximately 2°C below boiling to prevent splattering. Dry evaporated sample for at least 1 h in an oven at 103 to 105°C, cool dish in desiccator to balance temperature, and weigh. Repeat cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained, or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less. When weighing dried sample, be alert to change in weight due to air exposure and/or sample degradation. Duplicate determinations should agree within 5% of their average.

4. Calculation

$$\text{mg total solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

where:
   A = weight of dried residue + dish, mg, and
   B = weight of dish, mg.

5. Precision

Single-laboratory duplicate analyses of 41 samples of water and wastewater were made with a standard deviation of differences of 6.0 mg/L.

6. Bibliography

SYMONS, G.E. & B. MOREY. 1941. The effect of drying time on the determination of solids in sewage and sewage sludges. *Sewage Works J.* 13:936.

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* Vycor, product of Corning Glass Works, Corning, N.Y., or equivalent.
† Kimble Nos. 37005 or 37034B, or equivalent.

2540 SOLIDS*

2540 A. Introduction

The terms "solids," "suspended," and "dissolved," as used herein, replace the terms "residue," "nonfiltrable," and "filtrable" of editions previous to the 16th. Solids refer to matter suspended or dissolved in water or wastewater. Solids may affect water or effluent quality adversely in a number of ways. Waters with high dissolved solids generally are of inferior palatability and may induce an unfavorable physiological reaction in the transient consumer. For these reasons, a limit of 500 mg dissolved solids/L is desirable for drinking waters. Highly mineralized waters also are unsuitable for many industrial applications. Waters high in suspended solids may be esthetically unsatisfactory for such purposes as bathing. Solids analyses are important in the control of biological and physical wastewater treatment processes and for assessing compliance with regulatory agency wastewater effluent limitations.

1. Definitions

"Total solids" is the term applied to the material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature. Total solids includes "total suspended solids," the portion of total solids retained by a filter, and "total dissolved solids," the portion that passes through the filter.

The type of filter holder, the pore size, porosity, area, and thickness of the filter and the physical nature, particle size, and amount of material deposited on the filter are the principal factors affecting separation of suspended from dissolved solids. "Dissolved solids" is the portion of solids that passes through a filter of 2.0 μm (or smaller) nominal pore size under specified conditions. "Suspended solids" is the portion retained on the filter.

"Fixed solids" is the term applied to the residue of total, suspended, or dissolved solids after heating to dryness for a specified time at a specified temperature. The weight loss on ignition is called "volatile solids." Determinations of fixed and volatile solids do not distinguish precisely between inorganic and organic matter because the loss on ignition is not confined to organic matter. It includes losses due to decomposition or volatilization of some mineral salts. Better characterization of organic matter can be made by such tests as total organic carbon (Section 5310), BOD (Section 5210), and COD (Section 5220).

"Settleable solids" is the term applied to the material settling out of suspension within a defined period. It may include floating material, depending on the technique (2540F.3b).

2. Sources of Error and Variability

Sampling, subsampling, and pipeting two-phase or three-phase samples may introduce serious errors. Make and keep such samples homogeneous during transfer. Use special handling to insure sample integrity when subsampling. Mix small samples with a magnetic stirrer. If suspended solids are present, pipet with wide-bore pipets. If part of a sample adheres to the sample container, consider this in evaluating and reporting results. Some samples dry with the formation of a crust that prevents water evaporation; special handling is required to deal with this. Avoid using a magnetic stirrer with samples containing magnetic particles.

The temperature at which the residue is dried has an important bearing on results, because weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, and gases from heat-induced chemical decomposition, as well as weight gains due to oxidation, depend on temperature and time of heating. Each sample requires close attention to desiccation after drying. Minimize opening desiccator because moist air enters. Some samples may be stronger desiccants than those used in the desiccator and may take on water.

Residues dried at 103 to 105°C may retain not only water of crystallization but also some mechanically occluded water. Loss of CO_2 will result in conversion of bicarbonate to carbonate. Loss of organic matter by volatilization usually will be very slight. Because removal of occluded water is marginal at this temperature, attainment of constant weight may be very slow.

Residues dried at $180 \pm 2°C$ will lose almost all mechanically occluded water. Some water of crystallization may remain, especially if sulfates are present. Organic matter may be lost by volatilization, but not completely destroyed. Loss of CO_2 results from conversion of bicarbonates to carbonates and carbonates may be decomposed partially to oxides or basic salts. Some chloride and nitrate salts may be lost. In general, evaporating and drying water samples at 180°C yields values for dissolved solids closer to those obtained through summation of individually determined mineral species than the dissolved solids values secured through drying at the lower temperature.

To rinse filters and filtered solids and to clean labware use Type III water. Special samples may require a higher quality water; see Section 1080.

Results for residues high in oil or grease may be questionable because of the difficulty of drying to constant weight in a reasonable time.

To aid in quality assurance, analyze samples in duplicate. Dry samples to constant weight if possible. This means multiple drying-cooling-weighing cycles for each determination.

Analyses performed for some special purposes may demand deviation from the stated procedures to include an unusual constituent with the measured solids. Whenever such variations of technique are introduced, record and present them with the results.

3. Sample Handling and Preservation

Use resistant-glass or plastic bottles, provided that the material in suspension does not adhere to container walls. Begin analysis as soon as possible because of the impracticality of preserving

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Proximate and Ultimate Protocols

Standard Practice for
Proximate Analysis of Coal andd Coke[1]

This standard is issued under the fixed designation D 3172; the au 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. A superscript epsilon (ε) indicates an editorial change since the last rt revision or reapproval.

1. Scope

1.1 This practice covers the determination of moisture, volatile matter, and ash and the calculation of fixed carbon on coals and cokes sampled and prepared by prescribed methods and analyzed according to ASTM established procedures.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis[2]

D 388 Classification of Coals by Rank[2]

D 2013 Method of Preparing Coal Samples for Analysis[2]

D 2234 Test Methods for Collection of a Gross Sample of Coal[2]

D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke[2]

D 3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal[2]

D 3175 Test Method for Volatile Matter in the Analysis Sample of Coal and Coke[2]

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[1] This practice is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved Sept. 29, 1989. Published February 1990. Originally published as D 3172 – 73. Last previous edition D 3172 – 73(1984)ε¹.

[2] *Annual Book of ASTM Standards,* Vol 05.05.

3. Terminology

3.1 *Definition:*

3.1.1 *proximate analysis of coal and coke*—an assay of the moisture, ash, volatile matter, and fixed carbon as determined by prescribed methods. Other constituents such as sulfur and phosphorus are not included.

4. Significance and Use

4.1 Test methods, as herein described, can be used to establish the rank of coals, show the ratio of combustible to incombustible constituents, provide the basis for buying and selling, and evaluate for beneficiation or for other purposes.

5. Sampling

5.1 Coal sample collection shall be in accordance with Sections 5 and 6 of Classification D 388, if the proximate analysis is to be used for classification of coal by rank. In all other cases, sample collection shall be in accordance with Test Methods D 2234. Preparation shall be in accordance with Method D 2013. Coke sampling shall be in accordance with Method D 346.

6. Test Methods

6.1 *Moisture*—Test Method D 3173.

6.2 *Ash*—Test Method D 3174.

6.3 *Volatile Matter*—Test Method D 3175. If the modified procedure is required, the report should show that the modified procedure was used.

6.4 *Fixed Carbon*—The fixed carbon is a calculated value. It is the resultant of the summation of percentage moisture, ash, and volatile matter subtracted from 100. All percentages shall be on the same moisture reference base.

Fixed carbon, $\% = 100 - ($moisture, $\%$
$+$ ash, $\% +$ volatile matter, $\%)$

1

Standard Test Methods for
Sulfur in the Analysis Sample s of Coal and Coke Using High-Temperature Tube Furnace CCombustion Methods[1]

This standard is issued under the fixed designation D 4239; the lie number immediately following the designation indicates the year of original adoption or, in-tae case of revision, the year of last revivision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the lastast revision or reapproval.

1. Scope

1.1 These test methods cover three alternative procedures s using high-temperature tube furnace combustion methods ls for the rapid determination of sulfur in samples of coal and d coke.

1.2 These test methods appear in the following order:

1.2.1 When automated equipment is used to perform any y of the three methods of this test method, the procedures can n be classified as instrumental methods. There are several al manufacturers that offer to the coal industry equipment with h instrumental analysis capabilities for the determination of of the sulfur content of coal and coke samples.

1.3 *This standard does not purport to address all of the ue safety concerns, if any, associated with its use. It is the ue responsibility of the user of this standard to establish appro- priate safety and health practices and determine the applica- bility of regulatory limitations prior to use. See 7.8 and 15.2. 2.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 346 Practice for Collection and Preparation of Coke e Samples for Laboratory Analysis[2]

D 1193 Specification for Reagent Water[3]

D 2013 Method of Preparing Coal Samples for Analysis[2]

D 2361 Test Method for Chlorine in Coal[2]

D 3173 Test Method for Moisture in the Analysis Sample le of Coal and Coke[2]

D 3176 Practice for Ultimate Analysis of Coal and Coke[2] 2

D 3180 Practice for Calculating Coal and Coke Analyses s from As-Determined to Different Bases[2]

D 4208 Test Method for Total Chlorine in Coal by the e Oxygen Bomb Combustion/Ion Selective Electrode le Method[2]

D 4621 Guide for Accountability and Quality Control in n the Coal Analysis Laboratory[2]

D 5142 Test Methods for the Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures[2]

3. Summary of Test Methods

3.1 *Method A—High-Temperature Combustion Method with Acid-Base Titration Detection Procedures*—A weighed sample is burned in a tube furnace at a minimum operating temperature of 1350°C in a stream of oxygen. During combustion, all sulfur contained in the sample is oxidized to gaseous oxides of sulfur (sulfur dioxide, SO_2, and sulfur trioxide, SO_3) and the chlorine in the sample is released as Cl_2. These products are then absorbed into a solution of hydrogen peroxide (H_2O_2) where they dissolve forming dilute solutions of sulfuric (H_2SO_4) and hydrochloric (HCl) acids. The quantities of both acids produced are directly dependent upon the amounts of sulfur and chlorine present in the original coal sample. Once the amounts of each acid present have been determined, the percentage of sulfur contained in the coal may be calculated.

3.1.1 This method is written to include commercially available sulfur analyzers that must be calibrated with appropriate standard reference materials (SRMs) to establish recovery factors or a calibration curve based on the range of sulfur in the coal or coke samples being analyzed.

NOTE 1—Elements ordinarily present in coal do not interfere in Method A (3.1), with the exception of chlorine; results must be corrected for chlorine content of the samples (9.1).

3.2 *Method B—High-Temperature Combustion Method with Iodimetric Detection Procedures*—A weighed sample is burned in a tube furnace at a minimum operating tempera- ture of 1350°C in a stream of oxygen to ensure the oxidation of sulfur. The combustion products are absorbed in an aqueous solution that contains iodine. When sulfur dioxide is scrubbed by the diluent, the trace iodine originally present in the solution is reduced to iodide, thus causing an increase in resistance. The detection system of the instrument consists of a polarized dual platinum electrode. Any change in resistance of the solution in the vessel is detected. Iodine titrant is then added proportionally to the reaction vessel until the trace excess of iodine is replenished and the solution resistance is reduced to its initial level. The volume of titrant expended is used to calculate the sulfur concentration of the sample. The method is empirical; therefore, the apparatus must be calibrated by the use of standard reference materiel (SRM).

3.2.1 This method is designed to be used with commer- cially available sulfur analyzers, equipped to perform the preceding operation automatically, and must be calibrated

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with an appropriate sample (5.4) based on the range of sulfur in each coal or coke sample analyzed.

NOTE 2—Nonautomatic systems may be used with the titration procedures and calculations performed manually by qualified laboratory technicians. The resulting loss in accuracy or speed, or both, would then negate the advantages of using the fully automated instrumental approach.

3.3 *Method C—High-Temperature Combustion Method with Infrared Absorption Detection Procedures*—The sample is burned in a tube furnace at a minimum operating temperature of 1350°C in a stream of oxygen to oxidize the sulfur. Moisture and particulates are removed from the gas by traps filled with anhydrous magnesium perchlorate. The gas stream is passed through a cell in which sulfur dioxide is measured by an infrared (IR) absorption detector. Sulfur dioxide absorbs IR energy at a precise wavelength within the IR spectrum. Energy is absorbed as the gas passes through the cell body in which the IR energy is being transmitted: thus, at the detector, less energy is received. All other IR energy is eliminated from reaching the detector by a precise wavelength filter. Thus, the absorption of IR energy can be attributed only to sulfur dioxide whose concentration is proportional to the change in energy at the detector. One cell is used as both a reference and a measurement chamber. Total sulfur as sulfur dioxide is detected on a continuous basis. This method is empirical; therefore, the apparatus must be calibrated by the use of SRMs.

3.3.1 This method is for use with commercially available sulfur analyzers equipped to carry out the preceding operations automatically and must be calibrated using standard reference material (coal) of known sulfur content based on the range of sulfur in each coal or coke sample analyzed.

4. Significance and Use

4.1 Determination of sulfur is, by definition, part of the ultimate analysis of coal.

4.2 Results of the sulfur analysis are used to serve a number of interests: evaluation of coal preparation, evaluation of potential sulfur emissions from coal combustion or conversion processes, and evaluation of the coal quality in relation to contract specifications, as well as other scientific purposes.

4.3 The instrumental analysis provides a reliable, rapid method for determining the concentration of sulfur in a lot of coal or coke and are especially applicable when results must be obtained rapidly for the successful completion of industrial, beneficiation, trade, or other evaluations.

5. Sample

5.1 The sample shall be the material pulverized to pass No. 60 (250-μm) sieve and mixed thoroughly in accordance with Method D 2013 or Practice D 346.

NOTE 3—It may be difficult to meet the precision statements of Section 19 when high mineral content coals are ground to pass 60 mesh. When the precision of analysis required cannot be obtained, it is recommended that the coals be ground to pass through a No. 100 (150-μm) sieve. The reduced particle size should result in a more homogeneous sample.

5.2 A separate portion of the analysis sample should be analyzed for moisture content in accordance with Test Method D 3173, so that calculation to other than the as-determined basis can be made.

5.3 Procedures for converting as-determined sulfur values obtained from the analysis sample to other bases are described in Practices D 3176 and D 3180.

5.4 Standard Reference Material (SRM) such as SRM Nos. 2682 through 2685–*Sulfur in Coal* which consist of four different coals that have been individually crushed and ground to pass a 60-mesh sieve, and bottled in 50-g units, or other commercially available reference coals with a certified sulfur content.

METHOD A—HIGH-TEMPERATURE COMBUSTION METHOD WITH ACID-BASE TITRATION DETECTION PROCEDURES[5]

6. Apparatus

6.1 *Tube Furnace*—Capable of heating 150- to 175-mm area (hot zone) of the combustion tube (6.2) to at least 1350°C. It is usually heated electrically using resistance rods, a resistance wire, or molybdenum disilicide elements. Specific dimensions may vary with manufacturer's design.

NOTE 4—Induction furnace techniques may be used provided it can be shown that they meet the precision requirements of Section 19.

6.2 *Combustion Tube*—Approximately 28-mm internal diameter with a 3-mm wall thickness and 750 mm in length made of porcelain, zircon, or mullite. It must be gastight at working temperature. The combustion may be carried out in a tapered-end tube that is closely connected to the gas absorber by high temperature tubing with gastight joints. Acceptable configurations include connecting the tapered-end tube directly to the elbow of the fritted gas bubbler or to a 10/30 standard taper-ground joint that is attached to a heat resistant glass right angle bend. The temperature at the tapered end of the tube should be maintained high enough to prevent condensation in the tube itself.

6.2.1 Alternatively, a high-temperature straight refractory tube may be used, if available. It requires a silica adaptor (6.11) with a flared end that fits inside the combustion tube and serves as an exit for the gases.

6.3 *Flowmeter*, for measuring an oxygen flow rate up to 2.0 L/min.

6.4 *Sample Combustion Boats*, must be made of iron-free material and of a convenient size suitable for the dimensions of the instrument being used.

6.5 *Boat Puller*—Rod of a heat-resistant material with a bent or disk end to insert and remove boats from the combustion tube.

6.5.1 If the boat puller is to remain within the combustion tube while the boat is moved into the hot zone, it is necessary to pass the puller through a T-piece that is fitted into a rubber stopper at the inlet of the combustion tube. The open end of the T-piece is sealed with a rubber stopper to permit movement of the pusher and prevent escape of the oxygen

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[4] Available from the Office of Standard Reference Materials, Room B314, Chemistry Bldg., National Bureau of Standards, Washington, DC 20234.
[5] Based on the method of Mott, R. A., and Wilkinson, H. C., "Determination of Sulfur in Coal and Coke by the Sheffield High Temperature Method," *Fuel*, Fuel B, Vol. 35, 1956, p. 6. This method is designed for the rapid determination of sulfur in coal and coke. It is not applicable to coals or coal density fractions that have been subjected to treatment with chlorinated hydrocarbons because of the potentially high acidity of the combustion gases.

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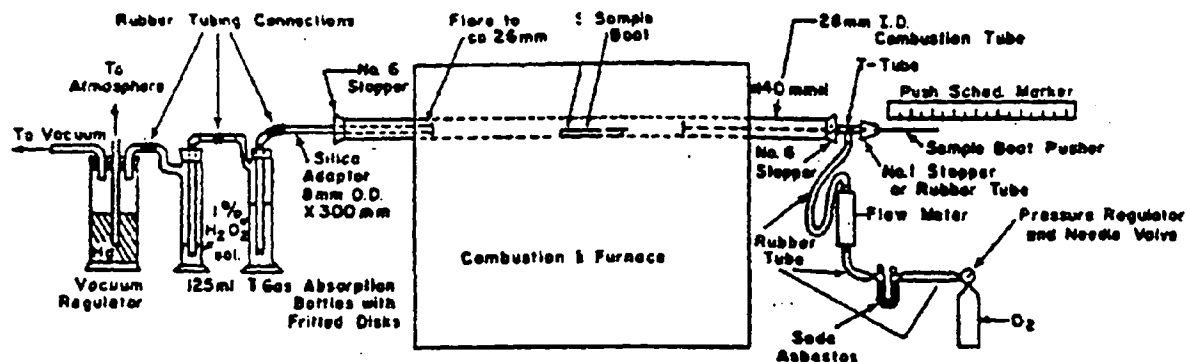
FIG. 1 Apparatus for the Determinanation of Sulfur Using Acid-Base Titration

·that enters at the side limb of the T. The rubber stopper or r tube should be checked often to avoid leakage.

6.6 *Gas Absorber or Analyzer Titration Vessel*—A narrow v vessel of such diameter that the end of the tube from which t the gasses exit is inside the vessel and submerged to a depth of at least 90 mm, when 200 mL of the peroxide solution (7.4) is added to the vessel.

6.6.1 Alternatively, 125-mL capacity bottles with fritted disk can be used for gas absorption. The bottles should be of such a diameter that the fritted end is covered by the peroxide solution to a depth of at least 50 mm. The fritted glass end porosity should be 15 to 40 μm. The bottles are fitted in a series of two to the outlet end of the combustion tube.

6.7 *Gas-Purifying Train*—Designed to be used with specific instruments, or a U-tube packed with soda asbestos may be used. See configuration in Fig. 1.

6.8 *Vacuum Source*—Needed if a negative pressure is used to transport the gasses and combustion products through the system.

6.9 *Vacuum Regulating Bottle*, containing mercury with an open-ended tube dipping into the mercury, used with a vacuum source.

6.10 *Silica Adaptor*, 300 mm long by 8 mm in outside diameter and flared at one end to 26 mm. To be used with a straight refractory combustion tube.

6.11 *Other Configurations of Apparatus*—Complete sulfur analyzer assembly units designed to perform functions similar to this method, with automated features that perform the sulfur analysis in a more rapid manner are commercially available. These instruments may have combustion tube dimensions and oxygen purifying apparatus that differ slightly from those described in this method, but are acceptable, provided equivalent values within the precision statement of Section 19 are obtained.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Available Reagents of the American Chem- l-

ical Society, where such specifications are available.[6] 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.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water, Type IV, conforming to Specification D 1193.

7.3 *Aluminum Oxide (Al_2O_3)*—finely divided and dried at 1350°C.

7.4 *Hydrogen Peroxide (H_2O_2) Solution*—One volume percent (50 mL of 30 % H_2O_2 with 1450 mL of water). The pH is adjusted (using NaOH or H_2SO_4 as appropriate) to that which is used for the end point in the titration. Solutions should be discarded after two or three days.

7.5 *Indicator*—Indicators that change color (titration end point) between pH 4 and 5 are recommended, but in no case should the pH exceed 7. Adequate lighting and stirring to ensure proper detection of the end point is essential. A choice of indicators or use of a pH meter is permitted (Note 5). Directions for preparing two acceptable mixed indicators are as follows:

7.5.1 Mix 1 part methyl red solution (dissolve 0.125 g in 60 mL of ethanol and dilute to 100 mL with water) with 3 parts bromcresol green solution (dissolve 0.083 g in 20 mL of ethanol and dilute to 100 mL with water). Discard the mixed solution after 1 week.

7.5.2 Mix equal volumes of methyl red solution (dissolve 0.125 g in 60 mL of ethanol and dilute to 100 mL with water) and methylene blue solution (dissolve 0.083 g in 100 mL of ethanol and store in a dark glass bottle). Discard the mixed solution after 1 week.

NOTE 5—Although two end-point indicators or a pH meter method are described, the use of the pH meter is accepted as more definitive of the end point of the titration process and considered to give more reproducible results.

7.6 *Soda-Asbestos*, 8 to 20 mesh, if a U-tube is used.

7.7 *Sodium Hydroxide, Standard Solution, 0.05N*—Dis-

[6] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

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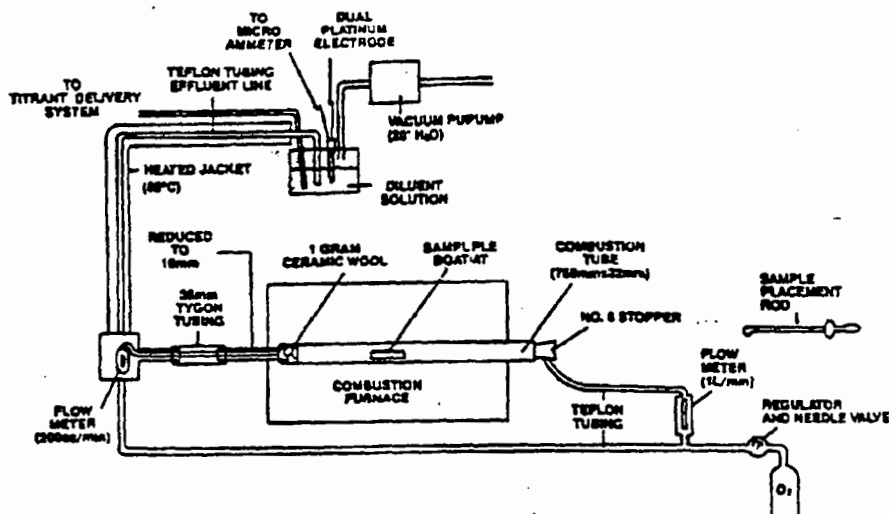
FIG. 2 Apparatus for the Determination of Sulfur by the Iodimetric Detection Method

solve 2.05 g of sodium hydroxide (NaOH) in water and dilute to 1 L. Standardize against a primary standard.

7.8 *Oxygen, 99.5 % Pure*—Compressed gas contained in a cylinder equipped with a suitable pressure regulator and a needle valve to control gas flow. Warning—Pure oxygen vigorously accelerates combustion. All regulators, lines, and valves should be free of grease and oil.

8. Procedure

8.1 Assemble the apparatus, as directed, by the instructions of the instrument manufacturer. Alternatively, the apparatus shown in Fig. 1 can be assembled except do not initially connect the rubber tube from the oxygen supply to the soda asbestos U-tube.

8.2 *Calibration*—Sulfur analyzers must be calibrated at least once on each day they are used, following the analysis procedure outlined in Section 8, using coal or coke standards (5.4) with sulfur values in the range of the samples being analyzed. A recovery factor (F) or calibration curve must be established and appropriately used in each calculation.

$$F = \frac{\text{Actual Sulfur in Standard, Dry Basis}}{\text{Analyzed Sulfur in Standard, Dry Basis}}$$

8.3 *Furnace Adjustment*—Raise the temperature of the furnace to at least 1350°C. Bring the temperature up slowly, allowing approximately 3 to 4 h in advance, to allow sufficient time to come to a stable temperature. Be sure to check the manufacturer's instructions for raising the temperature of the furnace and heed any precautions for protecting heating elements from deterioration or thermal shock.

8.4 *Titration Vessel Preparation*—Fill the titration vessel in accordance with the manufacturer's instructions with approximately 200 mL of the gas absorption fluid (hydrogen peroxide) (7.4). Adjust the pH of the solution to make it definitely acidic by adding dilute sulfuric acid. If chemical indicators (instead of a pH meter) are used, add five or six drops of the indicator and then add a very small quantity (as required) of dilute sodium hydroxide (NaOH) to reach the

end point color that will be developed in the sulfur analysis.

8.4.1 If the apparatus with two gas absorption bottles is used, add 100 mL of 1 % H_2O_2 (7.4) to the bottles so that at least 50 mm of the fritted disk is covered in the first bottle.

8.5 *Oxygen Flow*—Connect the oxygen supply and adjust the oxygen flow to approximately 2 L/min with the oxygen baffle inserted in the entrance end of the combustion tube. Be sure to check manufacturer's instructions. The flow rate at the temperature of 1350°C should be sufficient to prevent the formation of oxides of nitrogen. Allow the oxygen to flow through the combustion tube for at least 1 min before inserting any sample. Check the system for any possible leaks.

8.5.1 If a vacuum source is used, draw air through the apparatus at about 350 mL/min, then connect the oxygen supply to the U-tube and adjust the rate of flow of the oxygen to 300 mL/min. The flow rate is adjusted by changing the depth of the penetration into the mercury of the open-ended glass tube in the vacuum regulating bottle. The preliminary adjustment to 350 mL/min of air ensures that the connections at the outlet end of the combustion tube are under slightly reduced internal pressure and no leak of combustion products should occur.

Note 6—A gastight combustion train must be established with an adequate flow of approximately 300 mL/min of pure acid-free oxygen prior to analyzing samples on the equipment. This is best accomplished during the period the high-temperature tube furnace is brought to its operating temperature of 1350°C. The required gas flow may be established by the use of reduced internal pressure, or should the manufacturer specify or the operator prefer, it can be obtained by the use of a positive pressure train operated at slightly above atmospheric pressure to obtain the required oxygen flow rate. In all cases, the instructions of the manufacturer of the equipment should be followed. This also applies to the addition of sufficient gas absorption fluid as well as to the assembly of the apparatus.

8.6 *Analysis Sample Size*—Weigh out 0.5 g of the analysis sample to the nearest 0.1 mg for coals containing up to 4.0 % sulfur, and 0.25 g to the nearest 0.1 mg of analysis sample for

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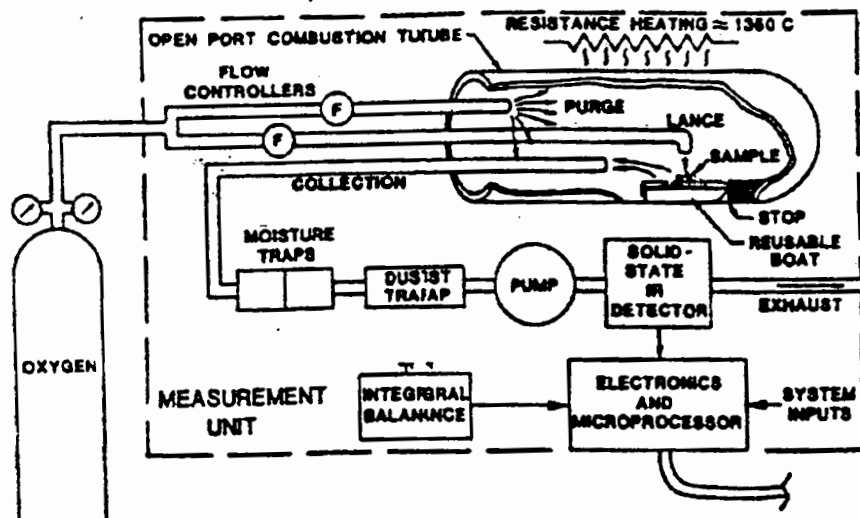
FIG. 3 Apparatus for the Determination of Sulfur by the Infrared Detection Method

coals containing over 4.0 % sulfur. Spread the sample evenly in a combustion boat.

8.6.1 A thin layer of Al_2O_3 can be used to line the sample boat and cover the sample to ensure complete combustion and reduce splattering or loss of sample.

8.7 *Sample Combustion*—Remove the oxygen baffle or rubber stopper or both from the combustion tube and put the charged sample boat into the inlet end of the combustion tube, approximately 270 mm from the center of the combustion tube hot zone. Close the combustion tube by replacing the oxygen baffle or rubber stopper or both and, if necessary, readjust the rate of flow of the oxygen. Leave the boat in this position for 1 to 3 min until the volatiles have been driven off. This will also eliminate the "popping" and soot accumulation in the right angle bend. Remove the oxygen baffle or rubber stopper and move the sample boat slowly forward until the boat is in the center of the hot zone, approximately 30 mm at the beginning of each minute for 6 min is the suggested schedule to ensure a slow heating rate. Be sure to remove the boat puller from the hot zone and replace the baffle or stopper after each movement. Allow the sample to burn in the hot zone for approximately 3 to 4 min until all sulfur in the sample is oxidized to sulfur dioxide (SO_2) or sulfur trioxide (SO_3). The complete sample burning time is not more than 14 to 15 min. This heating program has been established for all types of coal. Where it is shortened for a particular coal or by instruction of the manufacturer of a particular sulfur analyzer, results should be checked against those obtained by using the longer heating schedule.

8.7.1 If the rubber stopper with the T-piece is used (6.5.1), the rubber stopper remains in the end of the combustion tube and the boat puller is permitted movement into the furnace through the T-piece. See Fig. 1.

2.8 *Titration*—The gases of combustion leave the combustion tube through the exit end and are dissolved in the hydrogen peroxide in the gas absorption bottles or analyzer titration vessel forming a dilute sulfuric acid. Titrate the contents of this vessel with 0.05N sodium hydroxide (7.7),

backwashing the titration vessel and inlet tubes according to manufacturer's instructions. The total acidity, because of oxides of sulfur and chlorine, is given according to the following reactions:

$$SO_2 + H_2O_2 \rightarrow H_2SO_4$$
$$Cl_2 + H_2O_2 \rightarrow 2HCl + O_2$$
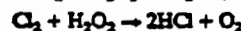
8.8.1 If the contents of the gas absorption bottles must be transferred to a suitable titration flask, be sure to wash the bottles and inlet tube or silica adaptor with water (7.2) and add these washings and five or six drops of indicator to the titration flask before titrating with the 0.05N NaOH solution (7.7).

8.8.2 High-temperature combustion acid/base titration sulfur analyzers may be designed to give a buret reading directly in percent sulfur content of the coal sample, but a correction still must be made for acidity caused by chlorine present in the sample using Test Methods D 2361 or D 4208.

NOTE 7—Often no correction is made for the presence of chlorine in the sample, or a percentage value (found as a relatively invariant value based upon prior knowledge of the coals being analyzed) is subtracted from the percent sulfur determined. This method can be acceptable for coals of known chlorine content; however, for work of the highest accuracy, the percentage of chlorine present in the sample must be determined analytically, and correction for its presence made by subtracting an equivalent value from a value equivalent to the total acidity determined by the sulfur titration.

9. Calculations

9.1 Some sulfur analyzers are designed to give buret readings in percent sulfur, if the titrant is adjusted and standardized to exactly 0.05N and the sample weight is exactly 0.500 g. After the observed percent sulfur has been adjusted using the recovery factor or calibration curve, then it must be corrected for chlorine using the following calculation:

$$S_c = 1.603 \ (S_b/1.603 \times F - Cl, \%/3.546)$$

where:

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S_c = sulfur corrected for chlorine (as determined), %;
S_b = sulfur from buret reading, %;
F = the recovery factor or factor taken from a calibration curve for the analyzer; and
Cl, % = chlorine in sample (as determined), %.

9.2 On analyzers that are designed to give buret readings in percent sulfur, but where the normality of the titrant or sample weight may vary from that prescribed, the following calculation must be used:

$$S_c = 1.603 \left[(S_b \times N_1 \times F \times 10) - Cl, \%/3.546 \right]/W$$

where:

S_c = sulfur corrected for chlorine (as determined), %;
S_b = sulfur taken from buret reading, %;
N_1 = normality of the sodium hydroxide;
F = recovery factor or factor taken from a calibration curve for the analyzer;
Cl, % = chlorine in sample (as determined), %; and
W = weight of sample, g.

9.3 When sulfur analyzers are used that have buret readings in millilitres of titrant, the following calculation will apply:

$$S_c = 1.603 \left[(V_1 \times N_1 \times F) - Cl, \%/3.546 \right]/W$$

where:

S_c = sulfur corrected for chlorine (as determined), %;
S_b = sulfur taken from buret reading, %;
V_1 = sodium hydroxide, mL;
N_1 = normality of sodium hydroxide;
Cl, % = chlorine in sample (as determined), %;
F = the recovery factor or factor taken from a calibration curve for the analyzer; and
W = weight of sample, g.

METHOD B—HIGH-TEMPERATURE COMBUSTION METHOD WITH IODIMETRIC TITRATION DETECTION PROCEDURES

10. Apparatus

10.1 *Analytical Apparatus*—Designed to perform the analysis procedure described in 3.2 automatically.

Note 8—It is recommended that the analytical equipment be an automated sulfur analyzer. Otherwise, the restrictions and limitations given in Note 3 for nonautomated systems apply.

10.2 *Tube Furnace*—See 6.1.

10.3 *Combustion Tube*—Made of mullite, porcelain, or zircon, approximately a 27-mm inner diameter, a 33-mm outer diameter, and 750 mm in length, with the last 23 mm of the exit end reduced to 10-mm outer diameter and 5-mm inner diameter to facilitate exit and collection of the gases in the titration vessel.

10.4 *Sample Combustion Boats*—See 6.4.

10.5 *Boat Puller*—See 6.5.

11. Reagents

11.1 *Purity of Reagents*—See 7.1.

11.2 *Purity of Water*—See 7.2.

11.3 *Iodine Titrant*—Dissolve 2.5 g of iodine in 280 mL of pyridine. Mix well and be certain all iodine is dissolved. Add 700 mL of methanol and 20 mL of water. (See Note 9.)

11.4 *Diluent*—Mix 280 mL of pyridine with 700 mL of methanol and 20 mL of water. Mix well.

Note 9—Alternative formulations may be substituted to the extent that they can be demonstrated to yield equivalent results in regard to accuracy and precision.

11.5 *Oxygen*—See 7.8.

12. Procedure

12.1 *Instrument Preparation:*

12.1.1 Assemble the analytical apparatus according to the manufacturer's instructions. Check all connections carefully to avoid leaks.

12.1.2 Set furnace temperature to 1350°C.

12.1.3 Set oxygen flow rate according to manufacturer's instructions.

12.1.4 Place approximately 150 mg of a coal sample in a boat and insert into the 1350°C region of the furnace. Sample boat should remain within the hot zone of the furnace for at least 2 min or until sample is completely burned. This action will serve to condition the apparatus in all functions.

12.2 *Calibration:*

12.2.1 Select a coal standard reference material (SRM), as described in 5.4, which has a sulfur value in the range of the sample to be analyzed. Weigh out about 150 mg of this previously dried coal standard and record the weight to the nearest 0.1 mg.

12.2.2 Enter the weight and sulfur content of the standard reference material sample into the memory of the analyzer.

12.2.3 Insert SRM sample into the 1350°C region of the furnace.

12.2.4 After endpoint is reached, not less than 2 min, record the titrant factor as milligrams sulfur per millilitre of titrant (mgS/mL). If analyzer does not have an integral computer, record the volume of titrant used and calculate titrant factor as instructed in 13.1.

12.2.5 Remove sample boat and repeat steps 12.2.1 through 12.2.4 two more times.

12.2.6 If analyzer does not automatically average the titrant factors obtained in the calibration step and enter the average into the microprocessor, then do so manually. Successive calibrations should yield titrant factors within 0.01 mgS/mL of each other.

12.3 *Analysis Procedure:*

12.3.1 Use an instrument that has been conditioned and calibrated according to 12.1 and 12.2.

12.3.2 Weigh to the nearest 0.1 mg, approximately 150 mg of the coal analysis sample into a boat.

12.3.3 Enter the sample weight into the sulfur analyzer memory.

12.3.4 Insert the coal sample into the 1350°C region of the furnace.

12.3.5 After the endpoint is reached (not less than 2 min) record the sulfur concentration of the sample. If analyzer does not have an integral computer, record the volume of titrant used and calculate the sulfur concentration as instructed in 13.2.

13. Calculations

13.1 On analyzers that do not calculate the titrant factor automatically, the following calculation must be used:

$$T = S_i \times W/100 \times V_i$$

where:
T = titrant factor, mg of sulfur/mL;
S_s = sulfur concentration of standard, dry basis;
W = weight of standard, mg; and
V_t = volume of titrant, mL.

13.2 On analyzers that do not calculate the percent sulfur ir in the analysis sample automatically, the following calcula-a-tion must be used:

$$S = 100 (T \times V_t)/W$$

where:
S = percent sulfur (as determined),
T = titrant factor (see 13.1),
V_t = volume of titrant, mL, and
W = weight of sample, mg.

METHOD C—HIGH-TEMPERATURE COMBUSTION METHOD WITH INFRARED ABSORPTION PROCEDURE

14. Apparatus

14.1 *Measurement Apparatus*—Equipped to combust the ie sample as described in 3.3 automatically. (See Note 8.)

14.2 *Tube Furnace*—See 6.1.

14.3 *Combustion Tube*—Made of mullite, porcelain, or or zircon with provisions for routing the gasses produced by iy combustion through the infrared cell.

14.4 *Sample Combustion Boats*—See 6.4.

14.5 *Boat Puller*—See 6.5.

15. Reagents

15.1 *Purity of Reagents*—See 7.1.

15.2 *Magnesium Perchlorate*—Warning: Magnesium n perchlorate is a strong oxidizing agent. Do not try to io regenerate the absorbent. Do not allow contact with organic ic materials or reducing agents.

15.3 *Oxygen*—See 7.8.

15.4 *Standard Reference Material (SRM)*—Such as SRM M Nos. 2682 through 2685—*Sulfur in Coal*,[7] reference coals or or calibrating agents with certified dry-basis sulfur values must st be used. The materials must be supplied by or have trace-a-ability to internationally recognized certifying organizations, s, such as the National Institute of Standards and Technology. y.

15.4.1 All SRMs, reference coals, or calibrating agents ts must have precision values of less than or equal to method id repeatability. Such SRMs, reference coals, or calibrating ig agents must be stable with respect to moisture and be ie pulverized to pass 100 % through a 0.250-mm (No. 60) USA A Standard Sieve. SRMs, reference coals, or calibrating agents ts must be mixed thoroughly before each use.

16. Procedure

16.1 *Instrument Preparation*—Perform system update te checks in accordance with manufacturer's instructions.

16.1.1 *Balance Calibration*—Calibrate internal balance in in accordance with manufacturer's instructions.

16.2 *Calibration of the Infrared Detection System*—Select ct SRMs, reference coals, or calibrating agents with known n dry-basis sulfur values in the range of the samples to be ie

[7] Available from the Office of Standard Reference Materials, Room B314, 4, Chemistry Bldg., National Institute of Standards and Technology, Washington, e, DC 20234.

analyzed. For the initial calibration and periodic verification of instrument linearity, at least three such SRMs, reference coals, or calibrating agents are recommended for each range of sulfur values to be tested. When performing a single point calibration (Note 10) the SRM, reference coal, or calibrating agent containing the highest sulfur value for the expected range should be used for calibration. The other two SRMs, reference coals, or calibrating agents should represent the low and midpoints of the expected range. When performing a multiple point calibration, two of the SRMs, reference coals, or calibrating agents should bracket the range of sulfur values to be tested with the third falling within the range. All results obtained must be within the allowable limits of the SRMs, reference coals, or calibrating agents. Records for all calibrations will be maintained in accordance with Guide D 4621.

16.2.1 All SRMs, reference coals, or calibrating agents used for calibrating the instrument should comply with the provisions of 15.4. CAUTION—An indicated problem with linearity of the instrument during calibration could result from contamination of the SRM, reference coal, or calibrating agent as the container becomes depleted. It is, therefore, suggested that extreme care be used in mixing the SRM, reference coal, or calibrating agent before removing any sample from the container and that it be discarded when less than 5 g remain in the container.

NOTE 10—When performing a single-point calibration, the technique of calibrating the instrument with the SRM, reference coal, or calibrating agent corresponding to the highest sulfur value expected for the range uses the optimum linear range available for calibration. Single-point calibration is most linear from the point of calibration to zero.

16.2.2 *Calibration Procedure*—Make a minimum of two determinations to condition the equipment before calibrating the system. The as-determined sulfur value of the SRM, reference coal, or calibrating agent used for calibration of the instrument must have been previously calculated from the certified dry-basis sulfur value and residual moisture determined using either Test Methods D 3173 or D 5142. Alternately, a quantity of the SRM, reference coal, or calibrating agent allocated to be used within a normal production period (Note 11) can be dried using either Test Methods D 3173 or D 5142, in which case, the dry basis sulfur value will be used. The dried material must be stored in a desiccator, and any remaining at the end of the normal production period must be discarded. Weigh five samples of the SRM, reference coal, or calibrating agent (Note 12) chosen to represent the range of sulfur values being tested. Follow the calibration procedure recommended by the manufacturer. For verification of the calibration curve, use SRMs, reference coals, or calibrating agents that bracket the range of values to be tested. All results obtained must be within the allowable limits of the SRMs, reference coals, or calibrating agents. Records for all calibrations will be maintained in accordance with Test Method D 4621.

NOTE 11—A normal production period would routinely be considered as 8-h shift. Dried SRMs, reference coals, or calibrating agents should not be maintained beyond one day for the purposes of instrument calibration. CAUTION—Previously dried material should not be redried as oxidation can readily occur.

NOTE 12—Weigh to the nearest 1.0 mg. Since the sulfur content of the SRMs, reference coals, or calibrating agents bracket the range of sulfur values being determined from the samples, the mass of the SRM,

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reference coals, or calibrating agents used for calibration and the samples to be analyzed should be approximately the same so that both materials produce about the same amount of infrared cell saturation (60 to 70 %).

16.2.3 *Periodic Calibration Verification*—On a periodic basis, verify the stability of the instrument and its calibration by analyzing a portion of the SRM, reference coal, or calibrating agent used to calibrate the instrument. The value determined for this material, when used as an unknown sample, must be within the certified value plus or minus the stated precision limits of the material. If the criteria for a successful verification of calibration in accordance with Test Method D 4621 is not met, the calibration procedure of 16.2.1 must be repeated and samples analyzed since the last successful verification must be repeated.

16.3 *Analysis Procedure*—Stabilize and calibrate the analyzer (see 16.2).

16.3.1 Raise the furnace temperature as recommended by the manufacturer to at least 1350°C. Weigh the sample (Note 12). Spread the sample evenly in a combustion boat and use a boat puller to position the sample in the hot zone of the furnace for at least 2 min (Note 13) or until completely combusted.

NOTE 13—The analytical cycle should begin automatically as soon as sulfur is detected.

16.3.2 When the analysis is complete, the instrument should indicate the sulfur value. Refer to the manufacturer's recommended procedure.

17. Report

17.1 The percent sulfur value obtained using any of the described methods is on an as-determined basis.

17.2 The results of the sulfur analysis may be reported on any of a number of bases, differing from each other in the manner by which moisture is treated.

17.3 Use the percentage of moisture in the sample passing a No. 60 (250-μm) sieve to calculate the as-determined results of the analysis sample to a dry basis.

17.4 Procedures for converting the value obtained on the analysis sample to other bases are described in Practices D 3176 and D 3180.

18. Precision and Bias

18.1 These are empirical methods that are highly dependent upon the calibration of the equipment, the closeness of the standards to the samples in sulfur content, chlorine content, iron content, and so forth.

18.2 *Precision Statement for High-Temperature Combustion Method Using Acid Base Titration Detection Procedures*—The relative precision of this method for the determination of total sulfur covers the concentration range from 0.5 to 6.0 %.

18.2.1 *Repeatability*—The difference in absolute value between two consecutive test results carried out on the same sample of 60-mesh pulp, in the same laboratory, by the same operator, using the same apparatus, should not exceed the repeatability interval $I(r)$ more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the repeatability interval, there is reason to question one or both of the test results. The repeatability interval may be calculated by use of the following equation:

$$I(r) = 0.06 + 0.03 \, \bar{X}$$

where $\bar{X}$ is the average of the two test results.

NOTE 14—This equation applies to the relative spread of a measurement that is expressed as a percentage and is derived from the statistical evaluation of the round-robin analytical results. *Example:* Duplicate analysis for total sulfur gave values of 1.52 and 1.57 %. The average sulfur of the duplicate analysis value is 1.55 % and the calculated repeatability $I(r)$ is 0.11. The difference between the two sulfur values is 0.05 and does not exceed the $I(r)$ of 0.11; therefore, these two values are acceptable at the 95 % confidence level.

18.2.2 *Reproducibility*—The difference in absolute value between the averages of replicate determinations, carried out in different laboratories on representative 60-mesh samples, prepared from the same bulk sample after the last stage of reduction, should not exceed the reproducibility interval $I(R)$ more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility interval, there is reason to question one, or both, of the test results. The reproducibility interval may be calculated by the use of the following equation:

$$I(R) = 0.03 + 0.11 \, \bar{X}$$

where $\bar{X}$ is the average of between-laboratory results.

NOTE 15—This equation applies to the relative spread of a measurement that is expressed as a percentage and is derived from the statistical evaluation of the round-robin analytical results. *Example:* Duplicate analysis for total sulfur in one laboratory gave an average value of 3.81 %, and a value of 4.00 % was obtained in a different laboratory. The between-laboratory average sulfur value is 3.91 %, the calculated $I(R)$ interval is 0.46 %, and the difference between the different laboratory values is 0.19 %. Since this difference is less than the $I(R)$, these two values are acceptable at the 95 % confidence level.

18.3 *Precision Statement for High-Temperature Combustion Method Using Iodimetric Detection Procedures*—The relative precision of this method for the determination of total sulfur covers the concentration range from 0.5 to 6.0 %.

18.3.1 *Repeatability*—The difference in absolute value between two consecutive test results carried out on the same sample of 60-mesh pulp, in the same laboratory, by the same operator, using the same apparatus should not exceed the repeatability interval $I(r)$ more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the repeatability interval, there is reason to question one, or both, of the test results. The repeatability interval may be determined by use of the following equation:

$$I(r) = 0.08 \, \bar{X}$$

where $\bar{X}$ is the average of the two test results.

NOTE 16—This equation applies to the relative spread of a measurement that is expressed as a percentage and is derived from the statistical evaluation of the round-robin analytical results. *Example:* Duplicate analysis for total sulfur gave values of 1.52 and 1.57 %. The average sulfur of the duplicate analysis value is 1.55 %, and the calculated repeatability interval $I(r)$ is 0.12. The difference between the two sulfur values is 0.05 and does not exceed the $I(r)$ of 0.12; therefore, these two values are acceptable at the 95 % confidence level.

18.3.2 *Reproducibility*—The difference in absolute value between the averages of replicate determinations, carried out in different laboratories on representative 60-mesh samples, prepared from the same bulk sample after the last stage of reduction, should not exceed the reproducibility interval $I(R)$ more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproduc-

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ibility interval, there is reason to question one, or both, of the
test results. The reproducibility interval may be determined
by use of the following equation:

$$I(R) = 0.08 + 0.09 \, \overline{x}$$

where $\overline{x}$ is the average of the between-laboratory results.

NOTE 17—This equation applies to the relative spread of a measurement that is expressed as a percentage and is derived from the statistical evaluation of the round-robin analytical results. *Example:* Duplicate analysis for total sulfur in one laboratory gave an average value of 3.81 %, and a value of 4.00 % was obtained in a different laboratory. The between-laboratory average sulfur value is 3.91 %, the calculated $I(R)$ interval is 0.43 %, and the difference between the different laboratory values is 0.19 %. Since this difference is less than the $I(R)$, these two values are acceptable at the 95 % confidence level.

18.4 *Precision Statement for High-Temperature Combustion Method Using Infrared Absorption Detection Procedures*

18.4.1 *Precision*—The relative precision of this test method for the determination of sulfur covers the concentration range from 0.28 to 5.61 %.

18.4.2 *Repeatability*—The difference in absolute value between two consecutive test results, carried out on the same sample in the same laboratory by the same operator using the same apparatus, should not exceed the repeatability interval (limit) $I(r)$ more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the repeatability interval (limit), there is reason to question one or both of the test results. The repeatability

interval on a dry basis may be determined by use of the following equation:

$$I(r) = 0.02 + 0.03 \, \overline{x}$$

where $\overline{x}$ is the average of the two test results (see Note 18).

18.4.3 *Reproducibility*—The difference in absolute value of replicate determinations, carried out in different laboratories on representative samples prepared from the same bulk sample after the last stage of reduction, should not exceed the reproducibility interval (limit) $I(R)$ more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility interval (limit), there is reason to question one or both of the test results. The reproducibility interval on a dry basis may be determined by use of the following equation:

$$I(R) = 0.02 + 0.09 \, \overline{x}$$

where $\overline{x}$ is the average of the two test results (see Note 18).

NOTE 18—These equations apply to the relative spread of a measurement that is expressed as a percentage as derived from a statistical evaluation of the round-robin results.

18.5 *Bias*—Bias is eliminated when the instrument is properly calibrated against certified reference standards. Proper calibration includes comparison of instrumental results to certified sulfur values. Results for certified standards above and below anticipated analysis sample results should be within certified precision levels for all standards over the calibration range for the instrument.

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Standard Test Methods for
Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal and Coke[1]

This standard is issued under the fixed designation D 5373; 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. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover the instrumental determination of carbon, hydrogen, and nitrogen in laboratory samples of coal and coke prepared in accordance with Test Methods D 2013 and D 346.

1.2 Within the limitations outlined below, these test methods are applicable to either the air-dry or moisture-free laboratory sample, or both.

1.2.1 For instrumental systems in which the moisture and waters of hydration in the sample are liberated with (and only with) the oxidation products upon combustion, the analyses can be performed on a test specimen of the air-dry sample (Note 1). Concentrations determined on this air-dried basis represent the total carbon (including that present as carbonate), total hydrogen (including that present as water), and total nitrogen.

NOTE 1—These systems are also satisfactory for determining the subject materials in the moisture-free sample.

1.2.2 For systems in which the moisture and hydrates are otherwise liberated, the analysis shall be performed on the moisture-free sample. Values obtained on this basis represent the total carbon, organic hydrogen, and total nitrogen.

1.3 These test methods can be used to provide for the requirements specified in Practice D 3176 for the ultimate analysis.

1.4 The values stated in SI units shall be regarded as the standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in 8.3.1.

2. Referenced Documents

2.1 *ASTM Standards:*

D 346 Test Method for Collection and Preparation of Coke Samples for Laboratory Analysis[2]

D 2013 Test Method for Preparing Coal Samples for Analysis[2]

D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke[2]

D 3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal[2]

D 3176 Practice for Ultimate Analysis of Coal and Coke[2]

D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases[2]

D 4621 Guide for Accountability and Quality Control in the Coal Analysis Laboratory[2]

D 5142 Test Methods for the Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures[2]

3. Summary of Test Methods

3.1 Carbon, hydrogen, and nitrogen are determined concurrently in a single instrumental procedure. In some systems, the procedure consists of simply weighing a test specimen, placing the test portion into the instrument, and initiating the (subsequently automatic) analytical process. In other systems, the analytical process may be controlled manually to some degree.

3.2 The actual process can vary substantially from instrument to instrument because a variety of means can be used to effect the primary requirements of the test methods. These test methods provide for the following: (1) conversion of the subject materials in an oxygen stream in their entirety to carbon dioxide, water vapor, nitrogen oxides, and ash respectively; and (2) subsequent, quantitative determination of the gases in an appropriate reference gas stream.

3.2.1 The conversion of the subject materials to their corresponding gases occurs largely during combustion of the sample at an elevated temperature in an atmosphere of purified oxygen. The gases that are produced include the following:

3.2.1.1 Carbon dioxide from the oxidation of organic and elemental carbon and the decomposition of carbonate minerals;

3.2.1.2 Hydrogen halides from organic halides (and organic hydrogen, as required);

3.2.1.3 Water vapor from the oxidation of (the remaining) organic hydrogen and the liberation of moisture and waters of hydration;

3.2.1.4 Nitrogen and nitrogen oxides from the oxidation of organic nitrogen and the decomposition of nitrates; and

3.2.1.5 Sulfur oxides from the oxidation of organic sulfur, and the decomposition of sulfide and sulfate minerals.

(1) In some systems, sulfurous and sulfuric acids can also be obtained from a combination of the sulfur oxides and the water vapor.

3.2.2 For hydrogen and nitrogen, the required conversion is completed in a two-step process consisting of the following:

[1] These test methods are under the jurisdiction of ASTM Committee D-5 on Coal and Coke and are the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

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[2] *Annual Book of ASTM Standards*, Vol 05.05.

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3.2.2.1 Removal of the halides and sulfur oxides and liberation of the associated hydrogen (as water), by conducting the combustion gases through a series of absorption traps containing appropriate absorbing materials.

3.2.2.2 Reduction of the nitrogen oxides to elemental nitrogen (see Note 2) by passing the resultant gases over copper at an elevated temperature. The carbon dioxide, water vapor, and nitrogen may then be determined via one of several satisfactory detection schemes.

Note 2—In this process, residual oxygen is also removed.

3.2.3 In one configuration, the gases are conducted through a series of thermal conductivity detectors and gas absorbers aligned so that, at the water vapor detector level, the gases pass through the sample side of the detector, a water vapor absorber, and the reference side of the detector. At the carbon dioxide detector level, the gases are then conducted through the sample side of the detector, a carbon dioxide absorber, and the reference side of the detector. Finally, the resultant gases, which contain only nitrogen and the carrier gas, pass through the sample side of the nitrogen detector and are vented. At this detector level, high-purity carrier gas is used as the reference gas. In these ways, the detectors determine the thermal conductivities solely of the specified components.

3.2.4 In a second configuration, the carbon dioxide and water vapor are determined by infrared detection, using an aliquot of the combustion gases from which only the halides and sulfur oxides have been removed. These detectors determine the infrared absorption of the pertinent gases at precise wavelength windows so that the absorbances result from only the specified components. In these systems, nitrogen is determined by thermal conductivity, using a second aliquot of the gases, additionally treated to also reduce the nitrogen oxides to nitrogen and to remove the residual oxygen, carbon dioxide, and water vapor.

3.2.5 In a third configuration, which is essentially a modified gas chromatographic system, the nitrogen, carbon dioxide, and water vapor in the treated combustion gases are eluted from a chromatographic column and determined (at appropriate retention times) by thermal conductivity detection.

3.3 In all cases, the concentrations of carbon, hydrogen, and nitrogen are calculated as functions of the following:

3.3.1 Measured instrumental responses,

3.3.2 Values for response per unit mass for the elements (established via instrument calibration), and

3.3.3 Mass of the sample.

3.4 Or to the following: the instrument response is proportional to the gas density, which has been calibrated against a gas density of known concentration.

3.5 A capability for performing these computations automatically can be included in the instrumentation used for these test methods.

4. Significance and Use

4.1 Carbon and hydrogen values are used to determine the amount of oxygen (air) required in combustion processes and for the calculations of efficiency of combustion processes.

4.2 Carbon and hydrogen determinations are used in

material balance calculations on coal conversion processes; also, one or the other is used frequently in correlations of chemical and physical properties, such as yields of products in liquefaction reactivity in gasification and the density and porosity of coal.

4.3 Nitrogen data are required to fulfill the requirements of the ultimate analysis, Practice D 3176. Also, the data obtained can be used to evaluate the potential formation of nitrogen oxides as a source of atmospheric pollution.

4.4 Nitrogen data are used for comparing coals and in research. If the oxygen content of coal is estimated by difference, it is necessary to make a nitrogen determination.

5. Apparatus

5.1 Because a variety of instrumental components and configurations can be used satisfactorily for these test methods, no specifications are presented here with respect to overall system design.

5.2 Functionally, however, the following requirements are specified for all approved instruments (Note 3):

Note 3—The approval of an instrument with respect to these functions is paramount to these test methods, since such approval tacitly provides approval of both the materials and the procedures used with the system to provide for these functions.

5.2.1 The conditions for combustion of the sample shall be such that (for the full range of applicable samples) the subject components shall be converted completely to carbon dioxide, water vapor (except for hydrogen associated with volatile halides), and nitrogen or nitrogen oxides. Generally, instrumental conditions that effect complete combustion include (1) availability of the oxidant, (2) temperature, and (3) time.

5.2.2 Representative aliquots of the combustion gases shall then be treated for the following reasons:

5.2.2.1 To liberate (as water vapor) hydrogen present as hydrogen halides and sulfur oxyacids; and

5.2.2.2 To reduce (to the element) nitrogen present as nitrogen oxides.

(1) The water vapor and nitrogen so obtained shall be included with the materials originally present in these aliquots.

5.2.3 Additional treatment of the test specimens (prior to detection) depends on the detection scheme used for the instrument (Note 4).

Note 4—The additional treatments can be provided by the instrumental components used to satisfy 5.2.2.

5.2.3.1 For the configuration described in 3.2.3, the halides proper, sulfur oxides, and residual oxygen shall be removed from the single test specimen in which the water vapor, carbon dioxide, and nitrogen are determined sequentially.

5.2.3.2 For the configuration described in 3.2.4, the test specimen in which the water vapor and carbon dioxide are determined, only the halides and sulfur oxides shall be removed from the gas stream in which the water vapor and carbon dioxide are determined. For combusted gases in which the nitrogen is determined, the water, carbon dioxide, and residual oxygen shall also be removed.

5.2.3.3 For the configuration described in 3.2.5, the halides and sulfur oxides shall be removed from the combusted

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gases obtained from the single test specimen.

5.2.4 The detection system (in its full scope) shall determine the analytical gases individually and without interference. Additionally, for each analyte, either of the following applies:

5.2.4.1 The detectors themselves shall provide linear responses that correlate directly to concentration over the full range of possible concentrations from the applicable samples, or

5.2.4.2 The system shall include provisions for evaluating nonlinear responses appropriately so that the nonlinear responses can be correlated accurately with these concentrations.

(*I*) Such provisions can be integral to the instrumentation, or they can be provided by (auxiliary) computation schemes.

5.2.5 Finally, except for those systems in which the concentration data are output directly, the instrument shall include an appropriate readout device for the detector responses.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] 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.

6.2 *Helium, Carrier Gas*, as specified by the instrument manufacturer.

6.3 *Oxygen*, as specified by the instrument manufacturer.

6.4 *Additional Reagents*, as specified by the instrument manufacturer. This specification refers to the reagents used to provide for the functional requirements cited in 5.2.2.2 through 5.2.3.3. These reagents can vary substantially for different instruments; in all cases, however, for systems that are functionally satisfactory (and therefore approved), the reagents recommended by the manufacturer are also tacitly approved. Consequently, these reagents shall be those recommended by the manufacturer.

7. Preparation of Analysis Sample

7.1 The samples shall initially be prepared in accordance with Test Methods D 2013 or D 346.

7.2 If required by characteristics of the instrumental system, reduce the air-dry samples (7.1) typically to pass 75 µm (No. 200 U.S.A. Standard Sieve Series) to obtain test units of the analysis sample in the size range recommended by the instrument manufacturer. If required by characteristics of the instrumental system, as specified in 1.2.2, treat the test specimens in accordance with Test Method D 3173 to provide moisture-free materials solely appropriate for these

[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Annular Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

systems. In this and all subsequent sample handling steps, exercise care to minimize changes in moisture content resulting from exposure to the atmosphere.

8. Instrument Preparation

8.1 Assemble the instrumental system in accordance with the manufacturer's instructions.

8.2 *Adjustment of Response of Measurement System*—Weigh an appropriate test portion of standard reference material (SRM), calibrating agent, or reference coal. Analyze the test portion (see 9.1). Repeat this procedure. Adjust instrument response, as recommended by the manufacturer, until the absence of drift is indicated.

8.3 *Calibration*—Select coal SRMs or other calibrating agents and materials specified by the manufacturer that have certified carbon, hydrogen, and nitrogen values in the range of samples to be analyzed. At least three such SRMs or calibrating agents are recommended for each range of carbon, hydrogen, and nitrogen values to be tested. When possible, two of the SRMs or calibrating agents shall bracket the range of carbon, hydrogen, and nitrogen to be tested, with the third falling within the range.

8.3.1 All coal SRMs should be in accordance with 7.1 and shall be supplied by or have traceability to an internationally recognized certifying organization. CAUTION: An indicated problem with linearity of the instrument during calibration can result from contamination of the SRM or calibrating agent as the container becomes depleted. It is therefore recommended that the SRM or calibrating agent be discarded when less than five grams remain in the container.

8.3.2 *Calibration Procedure*—Analyze, as samples, portions of an SRM, reference coal, or calibrating agent chosen to represent the level of carbon, hydrogen, and nitrogen in the samples to be tested. If not required by the characteristics of the instrumental system, use the "as-determined" carbon, hydrogen, and nitrogen values for calibration. These values must have been calculated previously from the certified "dry basis" carbon, hydrogen, and nitrogen values and residual moisture determined using either Test Methods D 3174 or D 5142. Continue analyzing until the results from five consecutive determinations fall within the repeatability interval (see 12.2.1) of these test methods. Calibrate the instrument according to the manufacturer's instructions using these values. Analyze, as samples, two SRMs reference coals or calibrating agents that bracket the range of values to be tested. The results obtained for these samples must be within the stated precision limits of the SRM, reference coal, or calibrating agent, or the calibration procedure must be repeated. Records for all calibrations must be in accordance with Guide D 4621.

8.3.3 *Periodic Calibration Verification and Recalibration*—In accordance with Guide D 4621, analyze a control sample on a periodic basis. Results obtained for the control sample must be within established limits, or all results obtained since the last successful control check must be rejected and the calibration procedure repeated.

9. Procedure

9.1 Analyze a test specimen of the analysis sample in accordance with the manufacturer's instructions.

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10. Calculation

10.1 Calculate the concentrations of carbon, hydrogen, and nitrogen, on the appropriate sample basis, as follows:

$$A = \frac{(B \times C)}{D} \times 100$$

where:

A = % of the analyte,

B = detector response for that analyte,

C = unit mass per detector response established for the analyte during calibration, and

D = mass of test specimen, g.

The calculations can be provided automatically by the instrumental system used for these test methods.

11. Report

11.1 Report results from the carbon, hydrogen, and nitrogen determinations on any of the several common bases that differ solely with respect to moisture. Procedures for converting the as-determined concentrations to the other bases are specified in Practices D 3176 and D 3180.

12. Precision and Bias

12.1 These test methods are highly dependent on the calibration of the equipment.

12.2 The precision of these test methods for the determination of carbon, hydrogen, and nitrogen was calculated from data obtained from coal and coke with the following concentration ranges: carbon (dry-basis) from 48.6 to 90.6 %, hydrogen (dry-basis) from 0.14 to 5.16 %, and nitrogen (dry-basis) from 0.69 to 1.57 %.

12.2.1 *Repeatability*—The difference, in absolute value, between two test results, conducted on portions of the same analysis sample, in the same laboratory, by the same operator, using the same apparatus, shall not exceed the repeatability interval $I(r)$ in more than 5 % of such paired values (95 % confidence level). When such a difference is

TABLE 1 Repeatability and Reproducibility

% Dry Basis	I(r)	I(R)
Carbon	0.64	2.51
Hydrogen	0.16	0.30
Nitrogen	0.11	0.17

found to exceed the repeatability interval, there is reason to question one, or both, of the test results. The repeatability intervals for carbon, hydrogen, and nitrogen are given in Table 1.

12.2.2 *Example*—Duplicate analyses for carbon exhibited values of 73.26 and 73.62 %. The absolute difference between the two test results is 0.36 %. Since this value does not exceed the $I(r)$ value of 0.64 %, these duplicate analyses are acceptable at the 95 % confidence level.

12.2.3 *Reproducibility*—The difference, in absolute value, between the averages of duplicate determinations conducted in different laboratories on representative samples prepared from the same bulk sample after reducing to 100 % through a 250 Mm (No. 60 U.S.A. Standard Sieve Series) sieve shall not exceed the reproducibility internal $I(R)$ in more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility interval, there is reason to question one, or both, of the test results. The reproducibility intervals for carbon, hydrogen, and nitrogen are given in Table 1.

12.2.4 *Example*—Duplicate analysis for hydrogen in one laboratory revealed an average value of 5.15 %, and a value of 4.93 % was obtained in a different laboratory. The difference between the different laboratory value is 0.22 %. Since the laboratory difference is less than the $I(R)$, the two laboratory results are acceptable at the 95 % confidence level.

12.3 *Bias*—Bias is eliminated when the apparatus is calibrated properly against certified reference standards. Proper calibration includes comparison of test data on NIST SRM 1632 or other reagents and materials that have certified carbon, hydrogen, and nitrogen values.

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Standard Test Method for
GROSS CALORIFIC VALUE (OF REFUSE-DERIVED FUEL BY THE BOMB CALORIMETER[1][1]

This standard is issued under the fixed designation E 711; the nunumber immediately following the designation indicates the year of original adoption or. in the case of revision. the year of last revisision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the ladast revision or reapproval.

1. Scope

1.1 This test method covers the determination of the gross calorific value of a prepared analysis sample of solid forms of refuse-derived fuel (RDF) by the bomb calorimeter method.

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific cautionary and precautionary statements see 6.10 and Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*
D 1193 Specification for Reagent Water[2]
D 3177 Test Method for Total Sulfur in the Analysis Sample of Coal and Coke[3]
E 1 Specification for ASTM Thermometers[4]
E 180 Practice for Determining the Precision Data of ASTM Methods for Analysis and Testing of Industrial Chemicals[5]
E 775 Test Methods for Total Sulfur in the Analysis Sample of Refuse-Derived Fuel[6]
E 790 Test Method for Residual Moisture in a Refuse-Derived Fuel Analysis Sample[6]
E 829 Method of Preparing RDF-3 Laboratory Samples for Analysis[6]

3. Terminology

3.1 *Definitions:*

3.1.1 *calorific value*—the heat of combustion of a unit quantity of a substance. It may be expressed in joules per gram (J/g), British thermal units per pound (Btu/lb), or calories per gram (cal/g) when required.

NOTE 1—The unit equivalents are as follows:
1 Btu (International Table) = 1055.06 absolute joules
1 Calorie (International Table) = 4.1868 absolute joules
1 Btu/lb = 2.326 J/g
1.8 Btu/lb = 1.0 cal/g

3.1.2 *gross calorific value*—the heat produced by combustion of a unit quantity of solid fuel, at constant volume. in an oxygen bomb calorimeter under specified conditions such that all water in the products remains in liquid form.

3.1.3 *net calorific value*—a lower value calculated from the gross calorific value. It is equivalent to the heat produced by combustion of a unit quantity of solid fuel at a constant pressure of one atmosphere, under the assumption that all water in the products remains in the form of vapor.

3.2 *Descriptions of Terms Specific to This Method:*

3.2.1 *calorimeter*—describes the bomb, the vessel with stirrer, and the water in which the bomb is immersed.

3.2.2 *energy equivalent*—the energy required to raise the temperature (Note 2) of the calorimeter system 1°C (or 1°F) per gram of sample. This is the number that is multiplied by the corrected temperature rise in degrees and divided by the sample weight in grams to give the gross calorific value after thermochemical corrections have been applied.

[1] This test method is under the jurisdiction of ASTM Committee E-38 on Resource Recovery and is the direct responsibility of Subcommittee E 38.01 on Energy.
Current edition approved Aug. 28, 1987. Published October 1987.
[2] *Annual Book of ASTM Standards.* Vol 11.01.
[3] *Annual Book of ASTM Standards.* Vol 05.05.
[4] *Annual Book of ASTM Standards.* Vol 14.01.
[5] *Annual Book of ASTM Standards.* Vol 15.05.
[6] *Annual Book of ASTM Standards.* Vol 11.04.

NOTE 2—Temperature change is measured in thermal units. Temperature changes may also be recorded in electromotive force, ohms, or other units when other types of temperature sensors are used. Consistent units must be used in both the standardization and actual calorific determination. Time is expressed in minutes. Weights are measured in grams.

3.2.3 *refuse-derived fuels*—solid forms of refuse-derived fuels from which appropriate analytical samples may be prepared are defined as follows in *ASTM STP 832*:[*]

RDF-1—Wastes used as a fuel in as-discarded form with only bulky wastes removed.

RDF-2—Wastes processed to coarse particle size with or without ferrous metal separation.

RDF-3—Combustible waste fraction processed to particle sizes, 95 % passing 2-in. square screening.

RDF-4—Combustible waste fraction processed into powder form, 95 % passing 10-mesh screening.

RDF-5—Combustible waste fraction densified (compressed) into the form of pellets, slugs, cubettes, or briquettes.

4. Summary of Test Method

4.1 Calorific value is determined in this method by burning a weighed analysis sample in an oxygen bomb calorimeter under controlled conditions. The calorific value is computed from temperature observations made before and after combustion, taking proper allowance for thermometer and thermochemical corrections. Either isothermal or adiabatic calorimeter jackets may be used.

5. Significance and Use

5.1 The calorific value, or heat of combustion, is a measure of the energy available from a fuel. Knowledge of this value is essential in assessing the commercial worth of the fuel and to provide the basis of contract between producer and user.

6. Apparatus

6.1 *Test Room*—The apparatus should be operated in a room or area free of drafts that can be kept at a reasonably uniform temperature and humidity for the time required for the determination. The apparatus should be shielded from direct sunlight and radiation from other sources. Controlled room temperature and humidity are desirable.

6.2 *Oxygen Bomb*, constructed of materials that are not affected by the combustion process or products sufficiently to introduce measurable heat input or alteration of end products. If the bomb is lined with platinum or gold, all openings shall be sealed to prevent combustion products from reaching the base metal. The bomb shall be designed so that all liquid combustion products can be completely recovered by washing the inner surfaces. There shall be no gas leakage during a test. The bomb shall be capable of withstanding a hydrostatic pressure test to 21 MPa (3000 psig) at room temperature without stressing any part beyond its elastic limit.

6.3 *Calorimeter*, made of metal (preferably copper or brass) with a tarnish-resistant coating and with all outer surfaces highly polished. Its size shall be such that the bomb will be completely immersed in water when the calorimeter is assembled. It shall have a device for stirring the water thoroughly and at a uniform rate, but with minimum heat input. Continuous stirring for 10 min shall not raise the calorimeter temperature more than 0.01°C (0.02°F) starting with identical temperatures in the calorimeter, room, and jacket. The immersed portion of the stirrer shall be coupled to the outside through a material of low heat conductivity.

6.4 *Jacket*—The calorimeter shall be completely enclosed within a stirred water jacket and supported so that its sides, top, and bottom are approximately 10 mm from the jacket walls. The jacket may be arranged so as to remain at constant temperature or with provisions for rapidly adjusting the jacket temperature to equal that of the calorimeter for adiabatic operation. It shall be constructed so that any water evaporating from the jacket will not condense on the calorimeter.

6.5 *Thermometers*—Temperatures in the calorimeter and jacket shall be measured with the following thermometers or combinations thereof:

6.5.1 *Mercury-in-Glass Thermometers*, conforming to the requirements for Thermometers 116°C or 117°C (56°F or 57°F) as prescribed in Specification E 1. Other thermometers of equal or better accuracy are satisfactory. These thermometers shall be tested for accuracy against a known standard (preferably by the National Bu-

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[*] *Thesaurus on Resource Recovery Terminology, ASTM STP 832, ASTM, 1983, p 72.*

reau of Standards) at intervals no greater than 2.0°C (3.6°F) over the entire graduated scale. The maximum difference in correction between any two test points shall not be more than 0.02°C (0.04°F).

6.5.2 *Beckmann Differential Thermometer*, having a range of approximately 6°C in 0.01°C subdivisions reading upward and conforming to the requirements for Thermometer 115°C, as prescribed in Specification E 1. Each of these thermometers shall be tested for accuracy against a known standard at intervals no larger than 1°C over the entire graduated scale. The maximum difference between any two test points shall not be more than 0.02°C.

6.5.3 *Calorimetric-Type Platinum Resistance Thermometer, 25-*, tested for accuracy against a known standard.

6.5.4 *Other Thermometers*—A high precision electronic thermometer employing balanced thermistors or a quartz thermometer may be used, provided the temperature rise indication is accurate within ±0.003°C per 1°C rise.

6.6 *Thermometer Accessories*—A magnifier is required for reading mercury-in-glass thermometers to one tenth of the smallest scale division. This shall have a lens and holder designed so as to introduce no significant errors due to parallax. A Wheatstone bridge and galvanometer capable of measuring resistance to 0.0001 Ω are necessary for use with resistance thermometers.

6.7 *Sample Holder*—Samples shall be burned in an open crucible of platinum, quartz, or acceptable base-metal alloy. Base-metal alloy crucibles are acceptable if after a few preliminary firings the weight does not change significantly between tasks.

6.8 *Firing Wire* shall be 100 mm of No. 34 B & S nickel-chromium alloy wire or 100 mm of No. 34 B & S iron wire. Equivalent platinum or palladium wire may be used provided constant ignition energy is supplied, or measured, and appropriate corrections made.

6.9 *Firing Circuit*—A 6 to 16-V alternating or direct current is required for ignition purposes with an ammeter or pilot light in the circuit to indicate when current is flowing. A stepdown transformer connected to an alternating current lighting circuit or batteries may be used.

6.10 CAUTION: The ignition circuit switch shall be of momentary double-contact type, normally open, except when held closed by the op-

erator. The switch should be depressed only long enough to fire the bomb.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[8] 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.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water, Type III, conforming to Specification D 1193.

7.3 *Benzoic Acid, Standard (C_6H_5COOH)*—Use National Bureau of Standards SRM (Standard Reference Material) benzoic acid. The crystals shall be pelletized before use. Commercially prepared pellets may be used provided they are made from National Bureau of Standards benzoic acid. The value of heat of combustion of benzoic acid, for use in the calibration calculations, shall be in accordance with the value listed in the National Bureau of Standards certificate issued with the standard.

7.4 *Methyl Orange, Methyl Red, or Methyl Purple Indicator* may be used to titrate the acid formed in the combustion. The indicator selected shall be used consistently in both calibrations and calorific determinations.

7.5 *Oxygen*, free of combustible matter. Oxygen manufactured from liquid air, guaranteed to be greater than 99.5 % pure, will meet this requirement. Oxygen made by the electrolytic process may contain a small amount of hydrogen rendering it unfit without purification.

7.6 *Sodium Carbonate, Standard Solution (0.34 N)*—One millilitre of this solution should be equivalent to 20.0 J in the nitric acid (HNO_3) titration. Dissolve 18.02 g of anhydrous sodium carbonate (Na_2CO_3) in water and dilute to 1 L. The Na_2CO_3 should be previously dried for 24 h

[8] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. 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, NY, and the "United States Pharmacopeia."

at 105°C. The buret used for the HNO_3 titration shall be of such accuracy that estimations to 0.1 mL can be made. A more dilute standard solution may be used for higher sensitivity.

8. Precautions

8.1 Due to the origins of RDF in municipal waste, common sense dictates that some precautions should be observed when conducting tests on the samples. Recommended hygienic practices include use of gloves when handling RDF and washing hands before eating or smoking.

8.2 The following precautions are recommended for safe calorimeter operation:

8.2.1 The weight of solid fuel sample and the pressure of the oxygen admitted to the bomb must not exceed the bomb manufacturer's recommendations.

8.2.2 Bomb parts should be inspected carefully after each use. Threads on the main closure should be checked frequently for wear. The bomb should be returned to the manufacturer occasionally for inspection and possibly proof of firing.

8.2.3 The oxygen supply cylinder should be equipped with an approved type of safety device, such as a reducing valve, in addition to the needle valve and pressure gage used in regulating the oxygen feed to the bomb. Valves, gages, and gaskets must meet industry safety codes. Suitable reducing valves and adaptors for 2 to 3.5-MPa (300 to 500-psig) discharge pressure are obtainable from commercial sources of compressed gas equipment. The pressure gage shall be checked periodically for accuracy.

8.2.4 During ignition of a sample, the operator shall not permit any portion of his body to extend over the calorimeter.

9. Sampling[*]

9.1 RDF products are frequently nonhomogeneous. For this reason significant care should be exercised to obtain a representative laboratory sample for the RDF lot to be characterized.

9.2 The sampling method for this procedure should be based on agreement between the involved parties.

9.3 The laboratory sample must be air-dried and particle size reduced to pass a 0.5-mm screen as described in Method E 829.

10. Standardization

10.1 Determine the energy equivalent of the calorimeter as the average of a series of ten individual runs, made over a period of not less than 3 days or more than 5 days. To be acceptable, the standard deviation of the series shall be 6.9 kJ/°C (6.5 Btu/°C) or less (see Appendix X1, Table X1). For this purpose, any individual run may be discarded only if there is evidence indicating incomplete combustion. If this limit is not met, repeat the entire series until a series is obtained with a standard deviation below the acceptable limit.

10.2 The weights of the pellets of benzoic acid in each series should be regulated to yield the same temperature rise as that obtained with the various samples tested in the individual laboratories. The usual range of weight is 0.9 to 1.3 g. Make each determination in accordance with the procedure described in Section 11, and compute the corrected temperature rise, T, as described in 12.1. Determine the corrections for HNO_3 and firing wire as described in 12.2 and substitute into the following equation:

$$E = [(H)(g) + e_1 + e_3 + e_4] \times t$$

where:

E = energy equivalent, J/°C,

H = heat of combustion of benzoic acid, as stated in the National Bureau of Standards certificate, J/g,

g = weight of benzoic acid, g,

t = corrected temperature rise, °C,

e_1 = titration correction, J,

c_3 = fuse wire correction, J, and

e_4 = correction for ignition energy if measured and corrected for, J.

10.3 Standardization tests should be repeated after changing any part of the calorimeter and occasionally as a check on both calorimeter and operating technique.

11. Procedure

11.1 *Weight of Sample*—Thoroughly mix the analysis sample of solid fuel in the sample bottle, taking care that the heavies and lights (fluff) are distributed in the sample (Note 3). Carefully weigh approximately 1 g of the sample directly into the crucible in which it is to be burned or into a tared weighing scoop from which the sample is transferred to the crucible. Weigh the sample to the nearest 0.1 mg. Some form of compac-

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[*] ASTM Subcommittee E38.01 is currently in the process of developing procedures for sampling RDF-3 and the preparation of an analysis sample. The chairman of E38.01 should be contacted for details.

tion may be necessary to ensure satisfactory ignition and complete combustion.

NOTE 3—In the event segregation of the heavies and lights cannot be avoided. attempt to remove sample from the bottle in such a way that a representative sample is transferred.

NOTE 4—Perform the residual moisture determination of the sample simultaneously using Test Method E 790.

11.2 *Water in Bomb*—Add 1.0 mL of water to the bomb by a pipet. Before adding this water, rinse the bomb, and drain the excess water, and leave undried.

11.3 *Firing Wire*—Connect a measured length of firing wire to the ignition terminals with enough slack to allow the firing wire to maintain contact with the sample.

11.4 *Oxygen*—Charge the bomb with oxygen to a consistent pressure between 20 and 30 atm (2.03 and 3.04 MPa). This pressure must remain the same for each calibration and for each calorific determination. If, by accident, the oxygen introduced into the bomb should exceed the specified pressure, do not proceed with the combustion. Detach the filling connection and exhaust the bomb in the usual manner. Discard this sample.

11.5 *Calorimeter Water*—It is recommended that calorimeter water temperature be adjusted before weighing as follows:

11.5.1 *Isothermal Jacket Method*, 1.6 to 2.0°C (3.0 to 3.5°F) below jacket temperature (Note 4).

11.5.2 *Adiabatic Jacket Method*, 1.0 to 1.4°C (2.0 to 2.5°F) below room temperature.

NOTE 5—This initial adjustment will ensure a final temperature slightly above that of the jacket for calorimeters having an energy equivalent of approximately 10 200 J/K (2450 cal/°C). Some operators prefer a lower initial temperature so that the final temperature is slightly below that of the jacket. This procedure is acceptable, provided it is used in all tests, including standardization. Use the same amount (±0.5 g) of water in the calorimeter vessel for each test and for calibration. The amount of water (2000 g is usual) can be most satisfactorily determined by weighing the calorimeter vessel and water together on a balance. The water may be measured volumetrically if it is always measured at the same temperature. Tap water may be satisfactory for use in calorimeter bucket.

11.6 *Observations, Isothermal Jacket Method*—Assemble the calorimeter in the jacket and start the stirrer. Allow 5 min for attainment of equilibrium; then record the calorimeter temperatures (Note 6) at 1-min intervals for 5 min. Fire the charge at the start of the sixth minute

and record the time and temperature, T^a. Add to this temperature 60 % of the expected temperature rise, and record the time at which the 60 % point is reached (Note 5). After the rapid-rise period (about 4 to 5 min), record temperatures at 1-min intervals on the minute until the difference between successive readings has been constant for 5 min.

NOTE 6—Use a magnifier and estimate all readings (except those during the rapid rise period) to the nearest 0.002°C (0.005°F) when using ASTM Bomb Calorimeter Thermometer 56C (56F). Estimate Beckmann thermometer readings to the nearest 0.001°C. Tap mercurial thermometers with a pencil just before reading to avoid errors caused by mercury sticking to the walls of the capillary.

NOTE 7—When the approximate expected rise is unknown, the time at which the temperature reaches 60 % of the total can be determined by recording temperatures at 45, 60, 75, 90, and 105 s after firing and interpolating.

11.7 *Observations, Adiabatic Jacket Method*—Assemble the calorimeter in the jacket and start the stirrer. Adjust the jacket temperature to be equal to or slightly lower than the calorimeter, and run for 5 min to obtain equilibrium. Adjust the jacket temperature to match the calorimeter with ±0.01°C (0.02°F) and hold for 3 min. Record the initial temperature (Note 6) and fire the charge. Adjust the jacket temperature to match that of the calorimeter during the period of rise, keeping the two temperatures as nearly equal as possible during the rapid rise, and adjusting to within ±0.01°C (0.02°F) when approaching the final equilibrium temperature. Take calorimeter readings at 1-min intervals until the same temperature is observed in three successive readings. Record this as the final temperature. Do not record time intervals since they are not critical in the adiabatic method.

11.8 *Analysis of Bomb Contents*—Remove the bomb and release the pressure at a uniform rate, in such a way that the operation will require not less than 1 min. Examine the bomb interior and discard the test if unburned sample or sooty deposits are found. Carefully wash the interior of the bomb including the capsule with distilled or deionized water containing the titration indicator until the washings are free of acid. Collect the washings in a beaker and titrate the washings with standard carbonate solution. Remove and measure or weigh the combined pieces of unburned firing wire, and subtract from the original length or weight to determine the wire consumed

in firing. Determine the sulfur content of the sample by any of the procedures described in Test Methods E 775.

12. Calculations

12.1 *Temperature Rise in Isothermal Jacket Calorimeter*—Using data obtained as prescribed in 11.6, compute the temperature rise, T, in an isothermal jacket calorimeter as follows:

$$T = T_c - T_a - r_1(b - a) - r_2(c - b)$$

where:
T = corrected temperature rise,
a = time of firing,
b = time (to nearest 0.1 min) when the temperature rise reaches 60 % of total,
c = time at beginning of period in which the rate of temperature change with time has become constant (after combustion),
T_a = temperature at time of firing, corrected for thermometer error (Note 7),
T_c = temperature at time c, corrected for thermometer error (Note 7),
r_1 = rate (temperature units per minute) at which temperature was rising during 5-min period before firing, and
r_2 = rate (temperature units per minute) at which temperature was rising during the 5-min period after time c. If the temperature is falling, r_2 is negative and the quantity $r_2(c - b)$ is positive.

12.2 *Temperature Rise in Adiabatic Jacket Calorimeter*—Using data obtained as prescribed in 11.7 compute the corrected temperature rise, T, as follows:

$$T = T_f - T_a$$

where:
T = corrected temperature rise, °C or °F,
T_a = initial temperature when charge was fired, corrected for thermometer error (Note 8), and
T_f = final temperature corrected for thermometer error.

Note 8—With all mercury-in-glass thermometers, it is necessary to make the following corrections if the total heat value is altered by 12 J/g or more. This represents a change of 0.001°C (0.002°F) in a calorimeter using approximately 2000 g of water. The corrections include the calibration correction as stated on the calibration certificate, the setting correction for Beckman thermometers according to the directions furnished by the calibration authority, and the correction for emergent stem. Directions for these corrections are given in Appendix X2.

12.3 *Thermochemical Corrections* (Appendix X3)—Compute the following for each test:
e_1 = correction for the heat of formation of HNO_3, J. Each millilitre of standard alkali is equivalent to 20.0 J.
e_2 = correction for heat of formation of H_2SO_4, J
= 55.2 × percent of sulfur in sample × weight of sample, g.
e_3 = correction for heat of combustion of firing wire, J (Note 10)
= 9.6 J/cm or 5980 J/g for No. 34 B & S gage Chromel C
= 11.3 J/cm or 7330 J/g for No. 34 B & S iron wire.
e_4 = correction for ignition energy of platinum or palladium if measured and corrected for.

Note 9—There is no correction for platinum or palladium wire, provided the ignition energy is constant.

12.4 *Calorific Value*:
12.4.1 Calculate the gross calorific value (gross heat of combustion) as follows:

$$H_s = [(T)(E) - e_1 - e_2 - e_3 - e_4]/g$$

where:
H_s = gross calorific value, J/g,
T = corrected temperature rise as calculated in 12.1 or 12.2, °C or °F, consistent with the water equivalent value,
E = energy equivalent (see Section 10),
e_1, e_2, e_3, e_4 = corrections as prescribed in 12.3, and
g = weight of sample, g.
12.4.2 Calculate the net calorific value (net heat of combustion) as follows:

$$H_i = H_s - 23.96 (H \times 9)$$

where:
H_i = net calorific value (net heat of combustion), J/g,
H_s = gross calorific value (gross heat of combustion), J/g, and
H = total hydrogen, %.

13. Precision and Bias[10]

13.1 *Precision*—The standard deviations of individual determinations, in Btu/lb, are:

[10] Supporting data are available on loan from ASTM Headquarters. Request RR:E38-1000.

Average	Within-laboratory	Between-laboratories		Average	Within-laboratory	Between-laboratories
HHV-1:				9500	99.2	249.2
6400	27.1	135.5		9300	40.3	67.6
5200	48.8	239.6				
HHV-2:						
7900	32.3	118.0				
7400	38.1	227.8				
HHV-3:						
9700	111.3	290.4				

13.2 These precision estimates are based on an interlaboratory study conducted in accordance with Practice E 180.

APPENNDIXES

(Nonmandatoryy Information)

X1. CALCULATION OF STANDARD DEVIATIOONS FOR CALORIMETER STANDARDIZATION

X1.1 The example given in Table X1.1 illustrates the method of calculating standard deviations for calorimeter standardizations.

TABLE X1.1 Standard Deviations for Calorimeter Standardardization[a]

Standardization Number	Column A Water Equivalent, (Btu/lb) × (g/°C)	Column B Code to 4400 (Column A-4400)	Column C (Column B)^2
1	4412	12	144
2	4407	7	49
3	4415	15	225
4	4408	8	64
5	4404	4	16
6	4406	6	36
7	4409	9	81
8	4410	10	100
9	4412	12	144
10	4409	9	81
Sum		92	940

Average = t^2 = x/10 = (92/1/10) + 4400 = 4409
Variance = s^2 = Column C − − (Column B)^2/n/n − 1 = 940 − (92)^2/10/9 = 10.4
Standard deviation. s = Variiriance = 10.4 = 3.22

[a] In this example the values = of water equivalent are typical for a calorimeter calibrated at such that the water equivalent multiplied by the temperature e rise in °C/g of sample will give the calorific value of the sample in Btu/lb.

X2. THERMOMETHER CORRECTIONS

X2.1 It is necessary to make the following corrections in the event they result in an equivalent change of 0.001°C or more.

X2.1.1 Calibration Correction shall be made in accordance with the calibration certificate furnished by the calibration authority.

X2.1.2 Setting Correction is necessary for the Beckmann thermometer. It shall be made in accordance with the directions furnished by the calibration authority.

X2.1.3 Differential Emergent Stem Correction—

The calculation depends upon the way the thermometer was calibrated and how it is used. The following two conditions are possible:

(a) Thermometers Calibrated in Total Immersion and Used in Partial Immersion—This emergent stem correction is made as follows:

$$\text{Correction} = K (t_e - t_a)(t_e + t_a - L - T)$$

where:
K = 0.00016 for thermometers calibrated in °C.
   0.00009 for thermometers calibrated in °F.

L = scale reading to which the thermometer was immersed.
T = mean temperature of emergent stem,
t_a = initial temperature reading, and
t_c = final temperature reading.

NOTE X2.1: *Example*—Suppose the point L, to which the thermometer was immersed, was 16°C; its initial reading, t_a, was 24.127°C, its final reading, t_c, was 27.876°C, the mean temperature of the emergent stem, T, was 26°C,
then:

Differential stem correction

$$= 0.00016 \ (28 - 24) \ (28 + 24 - 16 - 26)$$
$$= +0.006°C$$

(b) Thermometers Calibrated and Used in Partial Immersion but at a Different Temperature than the

Calibration Temperature—This emergent stem correction is made as follows:

where: $\quad$ Correction = $K \ (t_c - t_a) \ (t_1 - t^*)$
K = 0.00016 for thermometers calibrated in °C,
$\quad$ 0.00009 for thermometers calibrated in °F,
t_a = initial temperature reading,
t_c = final temperature reading,
t_1 = observed stem temperature, and
t^* = stem temperature at which the thermometer was calibrated.

NOTE X2.2: *Example*—Suppose the initial reading, t_a, was 80°F, the final reading, t_c, was 86°F, and that the observed stem temperature, t_1, was 82°F, and the calibration temperature, t^*, was 72°F; then:

Differential stem correction

$$= 0.00009 \ (86 - 90)(82 - 72)$$
$$= 0.005°F$$

X3. THERMOCHEMICAL CORRECTIONS

X3.1 *Heat of Formation of Nitric Acid*—A correction (e^1, in 12.3) of 20 J is applied for each 1 mL of standard Na_2CO_3 solution used in the acid titration. The standard solution (0.34 N) contains 18.02 g of Na_2CO_3/L. This correction is based on assumption that all the acid titrated is HNO_3 formed by the following reaction: ½ N_2 (g + ¾ O_2 (g) + ½ H_2O (l) = HNO_3 (in 500 mol H_2O), and (2) the energy of formation of 1 mol of HNO_3 is approximately 500 mol of water under bomb conditions is 14.1 kcal/mol.[6] When H_2SO_4 is also present part of the correction for H_2SO_4 is contained in the e_1 correction and the remainder in the e_2 correction.

X3.2 *Heat of Formation of Sulfuric Acid*—By definition the gross calorific value is obtained when the product of the combustion of sulfur in the sample is SO_2 (g). However, in actual bomb combustion processes, the sulfur is found as H_2SO_4 in the bomb washings. A correction (e_2 in 12.4.1) of 55.2 J is applied for each percent of sulfur in the 1-g sample, that is converted to H_2SO_4. This correction is based upon the energy of formation of H_2SO_4 in solutions such as will be present in the bomb at the end of a combustion. This energy is taken as −70.5 kcal/mol.[11] A correction, of 2 × 14.1 kcal/mol of sulfur was applied in the e_1 correction, so the additional correction necessary is 70.5 − (2 × 14.1) = 42.3 kcal/mol or 5520 J of sulfur in the sample (55.2 J × weight of sample in grams × % sulfur in sample).

X3.2.1 The value of 5520 J/g of sulfur is based on a coal containing about 5 % sulfur and about 5 %

hydrogen. The assumption is also made that the H_2SO_4 is dissolved entirely in water condensed during combustion of the sample.[12] If a 1-g sample of such a fuel is burned, the resulting H_2SO_4 condensed with water formed on the walls of the bomb will have a ratio of about 15 mol of water to 1 mol of H_2SO_4. For this concentration the energy of the reaction,

$$SO_2 \text{ (g)} + ½O_2 \text{ (g)} + H_2O \text{ (l)}$$
$$= H_2SO_4 \text{ (in 15 mol } H_2O)$$
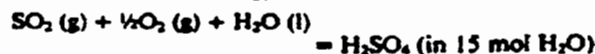
under the conditions of the bomb process is −70.5 kcal/mol.

X3.2.2 Basing the calculation upon a sample of comparatively large sulfur content reduces the overall possible errors, because for smaller percentages of sulfur the correction is smaller.

X3.3 *Fuse Wire*—Calculate the heat in SI units contributed by burning the fuse wire in accordance with the directions furnished by the supplier of the wire. For example, the heat of combustion of No. 34 B & S gage Chromel C wire is equivalent to 9.6 J/cm or 5980 J/g and that of No. 34 B & S gage iron wire is equivalent to 11.3 J/cm or 7330 J/g. There is no correction for platinum or palladium wire provided the ignition energy is constant.

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[11] Calculated from data in National Bureau of Standards Circular 500.
[12] Mott, R. A., and Parker, C., "Studies in Bomb Calorimetry IX-Formation of Sulfuric Acid," *Fuel*, Vol 37, 1958, p. 371.

X4. REPORTING RESULLTS IN OTHER UNITS

X4.1 *Reporting Results in British Thermal Units (Btu) per Pound*—The gross calorific value can be expressed in British thermal units by using the thermo-

chemical correction factors in Table X4.1 and the water equivalent expressed in (Btu/lb) × (g/°C).

TABLE X4.1 Thermochemical Correction Factors (Units in BTUU)

Correction	Multiplication Factor r	Multiply by
r_1 (HNO$_3$)	10.0	mL of 0.394 N Na$_2$CO$_3$ solution
r_2 (H$_2$SO$_4$)	23.7	% of sulfur in sample times weight of sample in grams
r_3 (fuse wire)	4.1 or	cm of No. 34 B & S gage Chromel C wire
	2570	weight (g) of Chromel C wire
r_3 (fuse wire)	4.9 or	cm of No. 34 B & S gage iron wire
	3150	weight (g) of iron wire

Designation: E 830 – 87

Standard Test Method for

ASH IN THE ANALYSIS SAMPLLE OF REFUSE-DERIVED FUEL[1]

This standard is issued under the fixed designation E 830; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revevision or reapproval.

1. Scope

1.1 This test method covers determination of the ash content in the analysis sample of refuse-derived fuel (RDF). The results obtained can be applied as the weight percent ash in the proximate analysis and in the ultimate analysis.

1.2 The values stated in acceptable metric units are to be regarded as standard. The values given in parentheses are for information only.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatcry limitations prior to use.* For specific precautionary statements see Section 6.

2. Referenced Documents

2.1 *ASTM Standards:*

E 180 Practice for Determining the Precision Data of ASTM Methods for Analysis and Testing of industrial Chemicals[2]

E 790 Test Method for Residual Moisture in a Refuse-Derived Fuel Analysis Sample[3]

E 829 Method of Preparing RDF-3 Laboratory Samples for Analysis[3]

3. Description of Term Specific to This Standard

3.1 *refuse-derived fuel*—Solid forms of refuse-derived fuels from which appropriate analytical samples may be prepared are defined as follows in *ASTM STP 832.*[4]

RDF-1—Wastes used as a fuel in as-discarded form with only bulky wastes removed.

P.DF-2—Wastes processed to coarse particle size with or without ferrous metal separation.

RDF-3—Combustible waste fraction processed to particle sizes, 95 % passing 2-in. square screening.

RDF-4—Combustible waste fraction processed into powder form, 95 % passing 10-mesh screening.

RDF-5—Combustible waste fraction densified (compressed) into the form of pellets, slugs, cubettes, or briquettes.

4.4. Summary of Test Method

4.1 Ash is determined by weighing the residue reremaining after burning the prepared analysis sasample under rigidly controlled conditions of sasample weight, temperature, and furnace atmospbphere.

5.5. Significance and Use

5.1 This test method is available to producers aand users of RDF as a method of determining ththe weight percent of ash in the analysis sample.

6.6. Apparatus

6.1 *Electric Furnace*—For determination of ththe ash content of RDF, the furnace shall have aadequate air ventilation and shall be capable of tetemperature regulation up to at least 750 ± 25°C. AAn air change rate of 1 to 4 furnace volumes of aiair per minute has been found adequate.

Note 1—It may be possible to reduce the rate of air

1

flow below the suggested minimum without adversely affecting results of the ash determination.

6.2 *Porcelain Capsules*, about 22 mm (⅞ in.) in depth, and 44 mm (1¾ in.) in diameter, or similar containers.

Note 2—Weighing bottles of borosilicate glass may be safely used without deformation or softening at temperatures of 600°C or less.

7. Precautions

7.1 Due to the origins of RDF in municipal waste, common sense dictates that some precautions should be observed when conducting tests on the samples. Recommended hygienic practices include use of gloves when handling RDF; wearing dust masks (NIOSH-approved type), especially while milling RDF samples; conducting tests under a negative pressure hood when possible; and washing hands before eating or smoking.

8. Sampling

8.1 The laboratory sample shall be obtained in accordance with sampling methods developed for materials of similar physical form.

8.2 The laboratory sample must be air-dried and particle size reduced to pass a 0.5-mm screen as described in Method E 829.

9. Procedure

9.1 After thoroughly mixing the analysis sample analysis sample to provide the best possible mix of heavy fines with the milled fluff, transfer approximately 1 g of the sample to a tared, previously fired container (weighed to the nearest 0.1 mg) with a scoop or spatula. Quickly weigh sample and container to the nearest 0.1 mg. As an alternate method use the dried analysis sample from the residual moisture determination. See Test Method E 790.

9.2 Place the uncovered container containing the sample in the furnace at low temperature and gradually heat to ignition at such a rate as to avoid mechanical loss from too rapid expulsion of volatile matter.

8.3 Finish the ignition to constant weight 9± 0.001 g/h) at 575 ± 25°C. It may be determined that a constant weight can be routinely established by allowing a sample to ash within the prescribed temperature range for a set period of time.

Note 3—Experience has shown that particles of glass and sand tend to sinter to each other and also to

p porcelain crucibles at temperatures close to 675°C. If laboratory conditions necessitate maintaining consistency in the maximum furnace temperature used for ash tests of other fuels, the ignition may be finished to constant weight (±0.001 g/h) at a temperature of 725 ± 25°C. If this option is invoked, it should be also noted that prolonged exposure to high temperatures may actually result in changes in weight due to possible chemical reactions.

9.4 Cool in a desiccator over desiccant and weigh as soon as possible after the container and ash reach the temperature of the area in which weighing is performed.

10. Calculations

10.1 Calculate the ash percent in the analysis sample as follows:

$$\text{Ash as-determined, } \% = [(A - B)/C] \times 100$$

where:
A = weight of container and ash residue, g,
B = weight of empty container, g, and
C = weight of ash analysis sample, g (includes residual moisture).

10.2 Use the numerical moisture value established by Test Method E 790 for converting ash data on the as-determined basis to the dry basis.

11. Report

11.1 Difficulty may be experienced in securing satisfactory check determinations of ash in the same or different laboratories for RDF rich in heavy fines. This is caused by siliceous matter such as glass and sand as well as a wide variety of other particles of different densities entrained in the milled RDF in nonuniform strata. When such a condition is anticipated or encountered, a paired set of determinations should be made, and the results reported as an average. If one determination of a paired set is accidentally ruined, another pair must be run. An off or unusual value does not constitute a ruined determination. In such cases, an additional set of duplicate determinations should be run and all values reported as an average of the two sets.

12. Precision and Bias

12.1 *Precision:*

12.1.1 The standard deviations of individual determinations in percent absolute are as follows:

Typical Average Value, %	Within-Laboratory, %	Between-Laboratories, %
20.0	0.6	1.3

2 :

12.1.2 These precision estimates are based on an interlaboratory study conducted in accordance with Practice E 180.

12.2 *Bias*—The bias of this test method cannot be determined due to the lack of a recognized standard reference material.

Standard Test Method for
Volatile Matter in the Analysis SSample of Refuse-Derived Fuel[1]

1. Scope

1.1 This test method covers the determination of the percentage of gaseous products, exclusive of moisture vapor, in the analysis sample which is released under specific conditions of the test. The knowledge of the volatile matter content assists in predicting burning characteristics of RDF.

1.2 This test method may be applicable to any waste material from which a laboratory analysis sample can be prepared.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*
E 180 Practice for Determining the Precision Data of ASTM Methods for Analysis and Testing of Industrial Chemicals[2]
E 790 Test Method for Residual Moisture in a Refuse-Derived Fuel Analysis Sample[3]
E 829 Test Method for Preparing RDF Laboratory Samples for Analysis[3]

3. Definition

3.1 *refuse-derived fuel* (RDF):
RDF-1—Waste used as a fuel in as-discarded form.
RDF-2—Waste processed to coarse particle size with or without ferrous metal separation.
RDF-3—shredded fuel derived from municipal solid waste (MSW) that has been processed to remove metal, glass, and other inorganics. This material has a particle size such that 95 weight % passes through a 2-in. square mesh screen.
RDF-4—Combustible waste processed into powder form—95 weight % passing a 10-mesh screen.
RDF-5—Combustible waste densified (compressed) into the form of pellets, slugs, cubettes or briquettes.
RDF-6—Combustible waste processed into liquid fuel.
RDF-7—Combustible waste processed into gaseous fuel.

4. Summary of Test Method

4.1 Volatile matter is determined by establishing the loss in weight resulting from heating refuse-derived fuel under rigidly-controlled conditions. The measured weight loss, corrected for moisture as determined in Test Method E 790, establishes the volatile matter content.

5. Apparatus

5.1 *Platinum or Fused Quartz Crucible,* with closely fitting cover. The crucible shall be of not less than 10 nor more than 20 mL capacity, not less than 25 nor more than 35 mm in diameter, and not less than 30 nor more than 35 mm in height.

5.2 *Vertical Electric Tube Furnace*—The furnace may be of the form shown in Fig. 1. It shall be regulated to maintain a temperature of $950 \pm 20°C$ in the crucible, as measured by a thermocouple positioned in the furnace.

6. Hazards

6.1 Due to the origins of RDF in municipal waste, common sense dictates that precautions should be observed when conducting tests on the samples. Recommended hygienic practices include use of gloves when handling RDF, wearing dust masks (NIOSH-approved type), especially while milling RDF samples, conducting tests under a negative-pressure hood when possible, and washing hands before eating or smoking.

NOTE 1—Caution—Exercise care when placing the sample into the volatile furnace. The possibility of an explosion always exists when heating samples of unknown origin.

7. Procedure

7.1 Weigh to the nearest 0.1 mg about 1 g of thoroughly mixed air-dried analysis RDF sample in a weighed crucible. Close with a cover (Note 2), place on a platinum or Nichrome-wire support and insert directly into the furnace chamber, which shall be maintained at a temperature of 950 $\pm$ 20°C. Lower the crucible immediately to the 950°C zone. Regulation of the temperature to within the prescribed limits is critical. After the more rapid discharge of volatile matter has subsided as shown by disappearance of the luminous flame, inspect the crucible to verify that the lid is still seated. If necessary, reseat the lid to guard against the admission of air into the crucible. Do this as rapidly as possible by raising the crucible to the top of the furnace chamber, reposition the lid to more perfectly seal the crucible, then lower immediately back to the 950°C zone.

NOTE 2—The cover should fit closely enough so that the carbon deposit from the refuse-derived fuel does not burn away from the underside.

[1] This test method is under the jurisdiction of ASTM Committee D-34 on Waste Management and is the direct responsibility of Subcommittee D34.13 on Waste Derived Fuels.
Current edition approved March 25, 1988. Published May 1988. Originally published as E 897 – 82. Last previous edition E 897 – 82.
[2] *Annual Book of ASTM Standards,* Vol 15.05.
[3] *Annual Book of ASTM Standards,* Vol 11.04.

7.2 After heating for a total of exactly 7 min, remove the crucible from the furnace and, without disturbing the cover, allow it to cool on a metal cooling block. Weigh as soon as cold (Note 3). The percentage loss of weight minus the percentage moisture in accordance with Test Method E 790 is the volatile matter.

NOTE 3—To ensure uniformity of results, the cooling period should be kept constant and should not be prolonged beyond 15 min.

8. Calculation

8.1 Calculate the percentage of volatile matter on an "as-determined" basis, V_{ad} as follows:

$$V_{ad} = \left[\frac{A - B}{A} \times 100\right] - M_{ad}$$

where:

A = weight of sample used, g,

B = weight of sample after heating, g, and

$M_{(ad)}$ = moisture (as-determined), %.

9. Precision and Bias

9.1 *Precision:*

9.1.1 The standard deviation of individual determinations, in percent absolute, is as follows:

Typical Average Value, 69 %
Within-Laboratory, 0.7 %
Between-Laboratories, 2.1 %

9.1.2 The precision estimates in 8.1.1 are based on an interlaboratory study conducted in accordance with Practice E 180.

9.2 *Bias:*

9.2.1 The bias of this test method has not been determined.

9.2.2 Precision estimates are based on ASTM Report No. RR:E 38-1000 which describes the preliminary testing and round-robin tests.[4]

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[4] Supporting data are available on loan from ASTM Headquarters. Request RR:E 38-1000.

Designation: E 949 – 88

Standard Test Method for
Total Moisture in a Refuse-Deriveed Fuel Laboratory Sample[1]

This standard is issued under the fixed designation E 949; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the measurement of the total moisture in RDF as it exists at the time it is sampled. Because of its empirical nature, strict adherence to test procedures are required for valid results. The standard is available to producers, vendors, and consumers as a total, two-stage moisture method.

1.2 Since RDF can vary from extremely wet (water saturated) to relatively dry, special emphasis must be placed on sampling, sample preparation, and the method of determination.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For hazard statement, see Section 7.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke[2]

E 790 Test Method for Residual Moisture in Refuse-Derived Fuel Analysis Sample[3]

E 829 Method of Preparing RDF Laboratory Samples for Analysis[3]

3. Definitions

3.1 *air drying*—a process of partial drying of RDF to bring its moisture content near to equilibrium with the atmosphere in which further reduction, division, and characterization of the sample are to take place. In order to bring about the equilibrium, the RDF is usually subjected to drying under controlled temperature conditions ranging from 30 to 40°C.

3.2 *analysis sample*—the final subsample prepared from the air-dried laboratory sample but reduced by passing through a mill with a 0.5 mm (0.02 in.) size or smaller final screen.

3.3 *bias*—a systematic error that is consistently negative or consistently positive. The mean of errors resulting from a series of observations that does not tend towards zero.

3.4 *gross sample*—a sample representing one lot and composed of a number of increments on which neither reduction

nor division has been performed.

3.5 *laboratory sample*—a representative portion of the gross sample received by the laboratory for analysis.

3.6 *lot*—a large designated quantity (greater than the quantity of the final sample) of RDF which can be represented by a a properly selected gross sample.

3.7 *precision*—a term used to indicate the capability of a person, an instrument, or a method to obtain reproducible results; specifically, a measure of the random error as expressed by the variance, the standard error, or a multiple of the standard error.

3.8 *forms of refuse-derived fuel (RDF):*

RDF-1—Wastes used as a fuel in as-discarded form.

RDF-2—Wastes processed to coarse particle size with or without ferrous metal separation.

RDF-3—shredded fuel derived from municipal solid waste (MSW) that has been processed to remove metal, glass, and other inorganics. This material has a particle size such that 95 weight % passes through a 2-in. (50-mm) square mesh screen.

RDF-4—Combustible waste processed into powder form, 95 weight % passing 10-mesh screening.

RDF-5—Combustible waste densified (compressed) into the form of pellets, slugs, cubettes, or briquettes.

RDF-6—Combustible waste processed into liquid fuel.

RDF-7—Combustible waste processed into gaseous fuel.

3.9 *representative sample*—a sample collected in such a manner that it has characteristics equivalent to the lot sampled.

3.10 *sample division*—the process of extracting a smaller sample from a sample so that the representative properties of the larger sample are retained. During this process it is assumed that no change in particle size or other characteristics occurs.

3.11 *sample preparation*—the process that includes drying, size reduction, division, and mixing of a laboratory sample for the purpose of obtaining an unbiased analysis sample.

3.12 *sample reduction*—the process whereby sample particle size is reduced without change in sample weight.

3.13 *significant loss*—any loss that introduces a bias in final results that is of appreciable importance to concerned parties.

4. Summary of Test Method

4.1 This test method is based on the loss in weight of RDF in an air atmosphere under controlled conditions of temperature, time, and air flow.

4.2 The laboratory sample is air-dried to near equilibrium with the atmosphere in the area where division and reduction will take place. The residual moisture determination is made in a heated, forced-circulation oven, under rigidly defined conditions.

[1] This test method is under the jurisdiction of ASTM Committee E-38 on Resource Recovery and is the direct responsibility of Subcommittee E38.01 on Energy.

Current edition approved March 25 1988. Published May 1988. Originally published as E 949 – 83. Last previous edition E 949 – 83.

[2] *Annual Book of ASTM Standards*, Vol 05.05.

[3] *Annual Book of ASTM Standards*, Vol 11.04.

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4.3 The total moisture is calculated from losses in air-drying and the residual moisture as shown in Section 11.

5. Significance and Use

5.1 The collection and treatment of the sample as specified herein is intended for the specific purpose of determining the total moisture in a laboratory sample of RDF.

5.2 This test method is available as the method for the determination of total moisture unless alternative techniques or modifications have been agreed upon by involved parties.

6. Apparatus

6.1 *Air Dry Moisture:*

6.1.1 *Drying Oven*—A large chamber mechanical draft oven capable of maintaining a controlled temperature in the range of 25 to 40°C. Air changes should be at the rate of 1 to 4 changes per minute. Air flow should be baffled to prevent samples from being blown out of the sample containers.

6.1.2 *Drying Pan*—A non-corroding pan or mesh basket to be used for holding the sample during air drying operations.

6.1.3 *Balance (Laboratory Sample)*—A balance of sufficient capacity to weigh the sample and container with a sensitivity of 0.5 g.

6.2 *Sample Reduction:*

6.2.1 *Mill*—A mill operating on the principle of cutting or shearing action shall be used for sample particle size reduction. It shall have the capability to regulate the particle size of the final product by means of either interchangeable screens or mill adjustments. The mill shall be enclosed and should generate a minimum amount of heat during the milling process to minimize the potential for loss of moisture. The final product shall pass through a 0.5 mm or smaller screen into a receiver integral with the mill. Access should be provided so that the mill can be cleaned quickly and easily between samples.

6.3 *Residual Moisture:*

6.3.1 *Drying Oven:*

6.3.1.1 *Referee Type*—The oven shall be so constructed as to have a uniform temperature within the specimen chamber, have a minimum excess air volume, and be capable of constant temperature regulation at 107 ± 3°C. Provision shall be made for renewing the preheated air in the oven at the rate of two to four times a minute, with the intake air dried by passing it through a desiccant. An oven similar to the one illustrated in Fig. 1, Moisture Oven, of Test Method D 3173 is suitable.

6.3.1.2 *Routine Type*—A drying oven of either the mechanical or natural circulation type which is capable of constant uniform temperature within the specimen chamber regulated at 107 ± 3°C.

NOTE 1—Either type of oven may be used for routine determinations. However, the referee-type oven shall be used to resolve differences between determinations.

6.3.2 *Containers*—A convenient form that allows the ash determination to be made on the same sample is a porcelain capsule 22 mm in depth and 44 mm in diameter or a fused silica capsule of similar shape. This shall be used with a well-fitting flat aluminum cover. Platinum crucibles or glass capsules with ground glass caps may also be used. They should be as shallow as possible consistent with convenient handleability.

6.3.3 *Analytical Balance*, with 0.1 mg sensitivity.

6.3.4 *Analysis Sample Containers*—Heavy (minimum 4 mil), vapor-impervious bags, properly sealed; or noncorroding cans, glass jars, or plastic bottles with air-tight sealing covers to store RDF samples for analysis. Containers shall be checked for suitability by measuring weight loss or gain of the sample and container stored for 1 week under ambient laboratory conditions. The weight loss or gain should be less than 0.5 % of the sample weight stored in container.

7. Hazards

7.1 Due to the origins of RDF in municipal waste, common sense dictates that some precautions should be observed when conducting tests on the samples. Recommended hygienic practices include use of gloves when handling RDF; wearing dust masks (NIOSH-approved type), especially when shredding RDF samples; conducting tests under negative pressure hood when possible; and when washing hands before eating or smoking.

7.2 Laboratory sample handling shall be performed by trained personnel. All operations shall be done as rapidly as possible to avoid sample moisture changes due to atmospheric exposure.

7.3 At all times RDF samples should be protected from moisture change due to exposure to rain, snow and sun, or contact with absorbent materials.

7.4 Since heavy fine particles tend to segregate rapidly in the RDF analysis sample, the analyst should exercise care to assure that the analysis sample is well mixed prior to performing the residual moisture determination.

7.5 When the residual moisture is to be used for the determination of total moisture, special care shall be taken to avoid any change in sample moisture between the completion of air drying and analysis for residual moisture. It is recommended that the delay between sample preparation and the determination of residual moisture be a maximum of 72 h.

7.6 Samples should be transported to the laboratory and analyzed as soon as possible. If any sample handling step involves an extended time period, the sample and container should be weighed before and after the process to determine any weight gain or loss. This weight gain or loss shall be included in the calculation of moisture content.

7.7 Force-feeding of the sample through the mill can overload the motor. An overload can cause rapid heating of the rotor and mill chamber with possible loss of residual moisture.

8. Sampling (Note 2)

8.1 RDF products are frequently nonhomogeneous. For this reason, care should be exercised to obtain a representative sample from the RDF lot to be characterized.

8.2 The sampling method for this procedure should be based on agreement between the involved parties.

8.3 For this procedure the laboratory sample size will normally not exceed 2 kg with some variation possible depending on the laboratory equipment available.

8.3.1 Due to the heterogeneous nature of RDF, dividing a laboratory sample to a very small size analysis sample may result in non-representative results. Since milling operations mix the sample as well as reduce particle size, laboratory

samples should not be divided before the initial preparation steps have been completed.

NOTE 2—ASTM Subcommittee E38.01 is currently in the process of developing a procedure for sampling RDF. The chairman of E38.01 should be contacted for details.

9. Sample Preparation

9.1 The principles, terms, organization and preparation procedures as established in Method E 829 shall apply to the handling and preparation of RDF for determination of total moisture by the two-stage method.

9.2 This procedure provides for using an air-drying oven to equilibrate laboratory sample moisture prior to reduction in size or amount and a moisture oven for determination of residual moisture on the air-dried analysis sample.

9.3 The laboratory sample must be air dried and particle size reduced to pass a 0.5 mm screen as described in Method E 829, for the residual moisture (second stage) of the total moisture determination.

10. Procedure

10.1 *Air Drying Laboratory Sample:*

10.1.1 Weigh the entire laboratory sample into a tared air-drying pan. Use more than one pan if necessary. If a very fine mesh type of drying pan is used, size the mesh such that the sample will not be lost through it. Sample depth in the drying pan shall be no greater than 10 cm (4 in) and any lumps of sample shall be broken up.

10.1.2 Air dry the sample at 10 to 15°C above ambient, but not greater than 40°C until the weight loss is less than 0.1 % of the sample weight per hour. Normally, allow the sample to air dry for a set time period such as overnight or 24 h. To speed the drying stage, stir the sample carefully while avoiding loss of sample (Note 3).

NOTE 3—The air discharge of the forced draft air drying oven should be filtered prior to discharge to minimize laboratory contamination by air entrained RDF dust.

10.1.3 At the end of the air drying period, cool the sample to room temperature and weigh. Protect the sample from contamination and loss during the cool-down process but do not place in a desiccator. Calculate air dry moisture loss percent in accordance with Section 11.

10.1.4 Separate, weigh, and hold non-millables for further classification and use for analysis if necessary (Note 4). Mill the remainder of the sample in accordance with Method E 829.

10.1.5 The calculation for the decimal percent of non-millables (*NM*) is:

$$NM = \frac{\text{Weight in grams of non-millables}}{\text{Weight in grams of air-dried sample}}$$

NOTE 4—Non-millables are those materials which will not pass through the milling screen, or may damage the milling apparatus, or

both.

10.2 *Residual Moisture on Air-Dried Analysis Sample*

10.2.1 Heat the empty containers and covers under the conditions at which the sample is to be dried, place the stopper or cover on the container, cool over a desiccant for about 15 to 20 min, and weigh. Mix the sample, if necessary, and dip out with a spoon or spatula from the sample bottle approximately 1 g of the sample. Put the sample quickly into the container, cover and weigh at once (Note 5).

NOTE 5—If weighing bottles with air-tight covers are used, it may not be necessary to preheat the moisture analysis container nor to desiccate it after drying.

10.2.2 Remove the cover and place in a desiccator. Quickly place the uncovered container into an oven preheated to 107 ± 3°C through which is passed a current of dry air. Close the oven at once and heat for 1 h. Open the oven, remove, cover the container quickly, and cool in a desiccator over desiccant. Weigh the sample and container as soon as cooled to room temperature.

11. Calculation

11.1 The air dry moisture, *A*, is calculated as follows:

$$A = \frac{G - L}{G} \times 100$$

where:
- A = air dry moisture, %,
- G = weight, in grams, of laboratory sample before air drying, and
- L = weight, in grams, of laboratory sample after air drying.

11.2 Calculate the percent residual moisture, *R*, in the analysis sample as follows:

$$R = \frac{S - B}{S} \times 100 \, (1 - NM)$$

where:
- R = residual moisture, %,
- S = grams of analysis sample used,
- B = grams of sample after heating at 107°C, and
- NM = decimal percent of non-millables as determined in 10.1.5.

11.3 Calculate the percent total moisture, *M*, in the laboratory sample, as follows:

$$M = \frac{R(100 - A)}{100} + A$$

where:
- M = total moisture, %,
- R = residual moisture, %, and
- A = air dry moisture, %

12. Precision and Bias

12.1 Precision and bias has not been determined.

N-7
pH and Temperature

4500-H⁺   pH VALUE*

4500-H⁺ A.   Introduction

1. Principles

Measurement of pH is one of the most important and frequently used tests in water chemistry. Practically every phase of water supply and wastewater treatment, e.g., acid-base neutralization, water softening, precipitation, coagulation, disinfection, and corrosion control, is pH-dependent. pH is used in alkalinity and carbon dioxide measurements and many other acid-base equilibria. At a given temperature the *intensity* of the acidic or basic character of a solution is indicated by pH or hydrogen ion activity. Alkalinity and acidity are the acid- and base-neutralizing capacities of a water and usually are expressed as milligrams CaCO₃ per liter. Buffer capacity is the amount of strong acid or base, usually expressed in moles per liter, needed to change the pH value of a 1-L sample by 1 unit. pH as defined by Sorenson[1] is $-\log[H^+]$; it is the "intensity" factor of acidity. Pure water is very slightly ionized and at equilibrium the ion product is

$$[H^+][OH^-] = K_w$$
$$= 1.01 \times 10^{-14} \text{ at } 25°C \qquad (1)$$

and

$$[H^+] = [OH^-]$$
$$= 1.005 \times 10^{-7}$$

where

$[H^+]$ = activity of hydrogen ions, moles/L,
$[OH^-]$ = activity of hydroxyl ions, moles/L, and
K_w = ion product of water.

Because of ionic interactions in all but very dilute solutions, it is necessary to use the "activity" of an ion and not its molar concentration. Use of the term pH assumes that the activity of

the hydrogen ion, a_{H^+}, is being considered. The *approximate* equivalence to molarity, $[H^+]$ can be presumed only in very dilute solutions (ionic strength <0.1).

A logarithmic scale is convenient for expressing a wide range of ionic activities. Equation 1 in logarithmic form and corrected to reflect activity is:

$$(-\log_{10} a_{H^+}) + (-\log_{10} a_{OH^-}) = 14 \qquad (2)$$

or

$$pH + pOH = pK_w$$

where:

pH† = $\log_{10} a_{H^-}$ and
pOH = $\log_{10} a_{OH^-}$.

Equation 2 states that as pH increases pOH decreases correspondingly and vice versa because pK_w is constant for a given temperature. At 25°C, pH 7.0 is neutral, the activities of the hydrogen and hydroxyl ions are equal, and each corresponds to an approximate activity of 10^{-7} moles/L. The neutral point is temperature-dependent and is pH 7.5 at 0°C and pH 6.5 at 60°C.

The pH value of a highly dilute solution is approximately the same as the negative common logarithm of the hydrogen ion concentration. Natural waters usually have pH values in the range of 4 to 9, and most are slightly basic because of the presence of bicarbonates and carbonates of the alkali and alkaline earth metals.

2. Reference

1. SORENSON, S. 1909. Über die Messung und die Bedeutung der Wasserstoff ionen Konzentration bei Enzymatischen Prozessen. *Biochem. Z.* 21:131.

* Approved by Standard Methods Committee, 1990.

† p designates $-\log_{10}$ of a number.

4500-H⁺ B.   Electrometric Method

1. General Discussion

a. Principle: The basic principle of electrometric pH measurement is determination of the activity of the hydrogen ions by potentiometric measurement using a standard hydrogen electrode and a reference electrode. The hydrogen electrode consists of a platinum electrode across which hydrogen gas is bubbled at a pressure of 101 kPa. Because of difficulty in its use and the potential for poisoning the hydrogen electrode, the glass electrode commonly is used. The electromotive force (emf) produced in the glass electrode system varies linearly with pH. This linear

relationship is described by plotting the measured emf against the pH of different buffers. Sample pH is determined by extrapolation.

Because single ion activities such as a_{H^+} cannot be measured pH is defined operationally on a potentiometric scale. The pH measuring instrument is calibrated potentiometrically with an indicating (glass) electrode and a reference electrode using National Institute of Standards and Technology (NIST) buffers having assigned values so that:

$$pH_s = -\log_{10} a_H$$

2550 TEMPERATURE*

2550 A.   Introduction

Temperature readings are used in the calculation of various forms of alkalinity, in studies of saturation and stability with respect to calcium carbonate, in the calculation of salinity, and

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in general laboratory operations. In limnological studies, water temperatures as a function of depth often are required. Elevated temperatures resulting from discharges of heated water may have significant ecological impact. Identification of source of water supply, such as deep wells, often is possible by temperature measurements alone. Industrial plants often require data on water temperature for process use or heat-transmission calculations.

2550 B.   Laboratory and Field Methods

1. Laboratory and Other Non-Depth Temperature Measurements

Normally, temperature measurements may be made with any good mercury-filled Celsius thermometer. As a minimum, the thermometer should have a scale marked for every 0.1°C, with markings etched on the capillary glass. The thermometer should have a minimal thermal capacity to permit rapid equilibration. Periodically check the thermometer against a precision thermometer certified by the National Institute of Standards and Technology (NIST, formerly National Bureau of Standards)* that is used with its certificate and correction chart. For field operations use a thermometer having a metal case to prevent breakage.

Thermometers are calibrated for total immersion or partial immersion. One calibrated for total immersion must be completely immersed to the depth of the etched circle around the stem just below the scale level.

2. Depth Temperature Measurements

Depth temperature required for limnological studies may be measured with a reversing thermometer, thermophone, or thermistor. The thermistor is most convenient and accurate; however, higher cost may preclude its use. Calibrate any temperature measurement devices with a NIST-certified thermometer before field use. Make readings with the thermometer or device immersed in water long enough to permit complete equilibration. Report results to the nearest 0.1 or 1.0°C, depending on need.

The thermometer commonly used for depth measurements is of the reversing type. It often is mounted on the sample collection

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apparatus so that a water sample may be obtained simultaneously. Correct readings of reversing thermometers for changes due to differences between temperature at reversal and temperature at time of reading. Calculate as follows:

$$\Delta T = \left[\frac{(T - t)(T + V_0)}{K} \right]$$
$$\times \left[1 + \frac{(T - t)(T + V_0)}{K} \right] + L$$

where:

ΔT = correction to be added algebraically to uncorrected reading,

T = uncorrected reading at reversal,

t = temperature at which thermometer is read,

V_0 = volume of small bulb end of capillary up to 0°C graduation,

K = constant depending on relative thermal expansion of mercury and glass (usual value of K = 6100), and

L = calibration correction of thermometer depending on T.

If series observations are made it is convenient to prepare graphs for a thermometer to obtain ΔT from any values of T and t.

3. Bibliography

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2560   PARTICLE COUNTING AND SIZE DISTRIBUTION (PROPOSED)*

2560 A.   Introduction

1. General Discussion

Particles are ubiquitous in natural waters and in-water and wastewater treatment streams. Particle counting and size distribution analysis can help to determine the makeup of natural waters, treatment plant influent, process water, and finished water. Similarly, it can aid in designing treatment processes, making decisions about changes in operations, and/or determining process efficiency. Methods for measuring particle size distribution included herein depend on electronic measurement devices because manual methods are likely to be too slow for routine analysis. However, when particle size analysis is to include size distribution of large (>500-μm) aggregates, use direct microscopic counting and sizing. Principles of various types of instruments capable of producing both size and number concentration information on particulate dispersions are included. Unless explicitly stated otherwise, the term "size distribution" means an absolute size distribution, i.e., one that includes the number concentration or count.

In most particle-counting instruments, particles pass though a sensing zone where they are measured individually; the only exception included is the static type of light-scattering instrument. Instruments create an electronic pulse (voltage, current, or resistance) that is proportional to a characteristic size of the particle. The instrument responses (pulse height, width, or area) are classified by magnitude and counted in each class to yield the particle size distribution.

2. Selection of Method

Three instrument types are included: electrical sensing zone instruments, light-blockage instruments, and light-scattering instruments.

Select instrument consistent with expected use of the particle size analysis. Instruments vary in the particle characteristic being sensed, lower and upper size limits of detection, degree of resolution of the size distribution, particle number concentration range that can be measured accurately, amount of shear to which a sample is subjected before measurement, amount of sample preparation, operator skill required, and the ease with which data can be obtained and manipulated into the desired forms. See Sections 2560B.1, C.1, and D.1, and manufacturers' literature for information on characteristics of each type of instrumentation.

Some instruments can be set up for either continuous-flow or batch sampling. Others can be used only for batch analysis. For instruments usable in both modes, check that no systematic differences in particle size distributions occur between continuous-flow measurements and batch samples taken at or near the intake point for continuous-flow samples.

3. Sample Collection and Handling

a. Batch samples: Use extreme care in obtaining, handling, and preparing batch samples to avoid changing total particle count and size distribution.

Choose representative times and locations for sampling. Ensure that particles are not subjected to greater physical forces during collection than in their natural setting. Collect samples from a body of water with submerged vessels to minimize turbulence and bubble entrainment. If sampling from particular depths, use standard samplers designed for that purpose. For flowing systems, make sure that the velocity into the opening of the sampling device is the same as that of the flowing stream (isokinetic sampling) and that the opening diameter is at least 50 times as large as the particles to be measured. For sampling from a tap, let water flow slowly and continuously down the side of the collection vessel.

Minimize particle contamination from the air, dilution water (or, for electrical sensing zone instruments, electrolyte solution) (see ¶ 4 below), and any vessel or glassware that comes in contact with the sample. Minimize exposure to air by keeping sample in a closed container and by minimizing time between sampling and analysis.

Preferably use glass bottles and other vessels with bottle cap liners of TFE.

Clean all glassware scrupulously by automatic dishwashing, vigorous hand brushing, and/or ultrasonication. Rinse glassware immediately before use with particle-free water. Between samples, rinse any part of the instrument that comes in contact with samples with either clean water or the upcoming sample. Alternatively, run multiple replicates and discard the first results.

To avoid breakup of aggregates of particles or flocs, sample and make dilutions very slowly using wide-bore pipets, needles, or other sampling devices; cut off pipet tips to avoid high velocities at the entrance. If sample dilution is required, add sample to dilution water, not vice versa, by submerging the pipet tip in the dilution water and releasing sample slowly. Use minimum intensity and duration of mixing adequate to dilute the suspension into the dilution water. Avoid mechanical stirrers inside the sample or ultrasonication. Simultaneously gently rotate and partially invert entire sample in a closed bottle. Use cylindrical dilution bottles to avoid sharp corners. Leave less than approximately 25% air space during mixing. To avoid sedimentation, make measurements immediately after mixing. Do not mix during measurement unless absolutely necessary to prevent sedimentation.

Most surface and ground waters contain relatively stable particles that aggregate slowly. Particle size distribution in biologically active waters or waters that have been treated with coagulants is more likely to change over short time periods. To minimize flocculation, minimize time between sampling and measurement. In highly flocculent systems, maximum holding time should be only a few minutes; for more stable samples, a few hours may be acceptable. Dilution slows flocculation kinetics

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N-8
CO Protocol

(See EPA Reference Method 10A, CFR 40, Part 60

N-9
CO_2 and O_2 Protocols

(See EPA Reference Method 3A, CFR 40, Part 60

N-10
Composite Sampling

Standard Guide for
Composite Sampling and Fieldd Subsampling for Environmental Waste Managenment Activities[1]

This standard is issued under the fixed designation D 6051; the se number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revidision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the lastst revision or reapproval.

1. Scope

1.1 Compositing and subsampling are key links in the chain of sampling and analytical events that must be performed in compliance with project objectives and instructions to ensure that the resulting data are representative. This guide discusses the advantages and appropriate use of composite sampling, field procedures and techniques to mix the composite sample and procedures to collect an unbiased and precise subsample(s) from a larger sample. It discusses the advantages and limitations of using composite samples in designing sampling plans for characterization of wastes (mainly solid) and potentially contaminated media. This guide assumes that an appropriate sampling device is selected to collect an unbiased sample.

1.2 The guide does not address: where samples should be collected (depends on the objectives) (see Guide D 6044), selection of sampling equipment, bias introduced by selection of inappropriate sampling equipment, sample collection procedures or collection of a representative specimen from a sample, or statistical interpretation of resultant data and devices designed to dynamically sample process waste streams. It also does not provide sufficient information to statistically design an optimized sampling plan, or determine the number of samples to collect or calculate the optimum number of samples to composite to achieve specified data quality objectives (see Practice D 5792). Standard procedures for planning waste sampling activities are addressed in Guide D 4687.

1.3 The sample mixing and subsampling procedures described in this guide are considered inappropriate for samples to be analyzed for volatile organic compounds. Volatile organics are typically lost through volatilization during sample collection, handling, shipping and laboratory sample preparation unless specialized procedures are used. The enhanced mixing described in this guide is expected to cause significant losses of volatile constituents. Specialized procedures should be used for compositing samples for determination of volatiles such as combining directly into methanolol (see Practice D 4547).

1.4 *This standard does not purport to address all of thehe safety concerns, if any, associated with its use. It is thehe responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

C 702 Practice for Reducing Samples of Aggregate to Testing Size[2]

D 1129 Terminology Relating to Water[3]

D 4439 Terminology for Geosynthetics[4]

D 4547 Practice for Sampling Waste and Soils for Volatile Organics[5]

D 4687 Guide for General Planning of Waste Sampling[5]

D 5088 Practice for Decontamination of Field Equipment Used at Nonradioactive Waste Sites[4]

D 5792 Practice for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives[5]

D 6044 Guide for Representative Sampling for Management of Wastes and Contaminated Media[3]

E 856 Definitions of Terms and Abbreviations Relating to Physical and Chemical Characteristics of Refuse-Derived Fuel[5]

3. Terminology

3.1 *Definitions:*

3.1.1 *composite sample, n*—a combination of two or more samples. **D 1129**

3.1.2 *sample, n*—a portion of material taken from a larger quantity for the purpose of estimating properties or composition of the larger quantity. **E 856**

3.1.3 *specimen, n*—a specific portion of a material or laboratory sample upon which a test is performed or which is taken for that purpose. **D 4439**

3.1.4 *subsample, n*—a portion of a sample taken for the purpose of estimating properties or composition of the whole sample.

3.1.4.1 *Discussion*—a subsample, by definition, is also a sample.

4. Summary of Guide

4.1 This guide describes how the collection of composite samples, as opposed to individual samples, may be used to: more precisely estimate the mean concentration of a waste analyte in contaminated media, reduce costs, efficiently determine the absence or possible presence of a hot spot (a highly contaminated local area), and, when coupled with retesting schemes, efficiently locate hot spots. Specific proce-

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dures for mixing a sample(s) and collecting subsamples for transport to a laboratory are provided.

5. Significance and Use

5.1 This guide provides guidance to persons managing or responsible for designing sampling and analytical plans for determining whether sample compositing may assist in more efficiently meeting study objectives. Samples must be composited properly, or useful information on contamination distribution and sample variance may be lost.

5.2 The procedures described for mixing samples and obtaining a representative subsample are broadly applicable to waste sampling where it is desired to transport a reduced amount of material to the laboratory. The mixing and subsampling sections provide guidance to persons preparing sampling and analytical plans and field personnel.

5.3 While this guide generally focuses on solid materials, the attributes and limitations of composite sampling apply equally to static liquid samples.

6. Attributes of Composite Sampling for Waste Characterization

6.1 In general, the individual samples to be composited should be of the same mass, however, proportional sampling may be appropriate in some cases depending upon the objective. For example, if the objective is to determine the average drum concentration of a contaminant, compositing equals volumes of waste from each drum would be appropriate. If the objective is to determine average contaminant concentration of the waste contained in a group of drums, the volume of each sample to be composited should be proportional to the amount of waste in each drum. Another example of proportional sampling is estimating the contaminant concentration of soil overlying an impermeable zone. Soil cores should be collected from the surface to the impermeable layer, regardless of core length.

6.2 The principal advantages of sample compositing include: reduction in the variance of an estimated average concentration (1),[6] increasing the efficiency of locating/identifying hot spots (2), and reduction of sampling and analytical costs (3). These main advantages are discussed in the following paragraphs. However, a principle assumption needed to justify compositing is that analytical costs are high relative to sampling costs. In general, appropriate use of sample compositing can:

6.2.1 Reduce inter-sample variance, that is, improve the precision of the mean estimation while reducing the probability of making an incorrect decision,

6.2.2 Reduce costs for estimating a total or mean value, especially where analytical costs greatly exceed sampling costs (also may be effective when analytical capacity is a limitation),

6.2.3 Efficiently determine the absence or possible presence of hot spots or hot containers and, when combined with retesting schemes, identify hot spots, as long as the probability of hitting a hot spot is low,

6.2.4 Be especially useful for situations, where the nature

⁶ The boldface numbers in parentheses refer to a list of references at the end of this guide.

of contaminant distribution tends to be contiguous and non-random and the majority of analyses are "non-detects" for the contaminant(s) of interest, and

6.2.5 Provide a degree of anonymity where population, rather than individual statistics are needed.

6.3 *Improvement in Sampling Precision*—Samples are always taken to make inferences to a larger volume of material, and a set of composite samples from a heterogeneous population provides a more precise estimate of the mean than a comparable number of discrete samples. This occurs because compositing is a "physical process of averaging." Averages of samples have greater precision than the individual samples. Likewise, a set of composite samples is always more precise than an equal number of individual samples. Decisions based on a set of composite samples will, for practical purposes, always provide greater statistical confidence than for a comparable set of individual samples.

6.3.1 If an estimated precision of a mean is desired, then more than one composite sample is needed; a standard deviation cannot be calculated from one composite sample. However, the precision of a single composite sample may be estimated when there are data to show the relationship between the precision of the individual samples that comprise the composite sample and that of the composite sample. The precision (standard deviation) of the composite sample is approximately the precision of the individual samples divided by the square root of the number of individual samples in the composite.

6.4 *Example 1*—An example of how a single composite sample can be used for decision-making purposes is given here. Assume a regulatory limit of 1 mg/kg and a standard deviation of 0.5 mg/kg for the individual samples. If the concentration of a site is estimated to be around 0.6 mg/kg, how many individual samples should be composited to have relatively high confidence that the true concentration does not exceed the regulatory limit when only one composite sample is used? Assuming the composite is well mixed, then the precision of a composite is a function of the number of samples as follows:

Number of Individual Samples in Composite	Precision (standard deviation ÷ $\sqrt{n}$) of One Composite Sample
2	0.35
3	0.29
4	0.25
5	0.22
6	0.20

Thus, if six samples are included in a composite, the composite concentration of 0.6 mg/kg is two standard deviations below the regulatory limit. Therefore, if the composite concentration is actually observed to be in the neighborhood of 0.6 mg/kg, we can be reasonably confident (approximately 95 %) that the concentration of the site is below the regulatory limit, using only one composite sample.

6.5 *Example 2*—Another example is when the standard deviation of the individual samples in the previous example is relatively small, say 0.1 mg/kg. Then the standard deviation of a composite of 6 individual samples is 0.04 mg/kg (0.1 mg/kg divided by the square root of 6 = 0.04 mg/kg), a very small number relative to the regulatory limit of 1 mg/kg. In this case, simple comparison of the composite concentration to the regulatory limit is often quite adequate for decision-making purposes.

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6.5.1 The effectiveness of compositing depends on thethe relative magnitude of sampling and analytical error. Whenen sampling uncertainty is high relative to analytical error (as is is usually assumed tc be the case) compositing is very effectiveve in improving precision. If analytical errors are high relativeve to field errors, sample compositing is much less effective.

6.5.2 Because compositing is a physical averaging process,ss, composite samples tend to be more normally distributededed than the individual samples. The normalizing effect ii is frequently an advantage since calculation of means, standardrd deviations and confidence intervals generally assume thdhe data are normally distributed. Although environmental res-es-idue data are commonly non-normally distributed, com-n-positing often leads to approximate normality and avoids thdhe need to transform the data.

6.5.3 The spatial design of the compositing scheme can bebe important. Depending upon the locations from which thehe individual samples are collected and composited, compositeces can be used to determine spatial variability or improve thehe precision of the parameter being estimated. Figures 1 and 2 2 represent a site divided into four cells. Composite all sampleles with the same number together. The sampling approach ir in Fig. 1 is similar to sample random sampling, except they arare now composite samples. Each composite sample in this casase is a representative sample of the entire site, eliminatetes cell-to-cell variability, and leads to increased precision ir in estimating the mean concentration of the site. If there is a a need to estimate the cell-to-cell variability, then the approacich in Fig. 2 is suitable. In addition, if the precision of estimatining the mean concentration of the cell is needed, multipiple composite samples should be collected from that cell.

6.6 *Effect on Cost Reduction*—Because the compositidte samples yield a more precise mean estimate than the samme number of individual samples, there is the potential fofor substantial cost saving. Given the higher precision associateted with composite samples, the number of composite sampleles required to achieve a specified precision is smaller than thahat required for individual samples. This cost saving opportunittity is especially pronounced when the cost of sample analysis i is high relative to the cost of sampling, compositing, anmd analyzing.

6.7 *Hot Container/Hot Spot Identification and Retestining Schemes*—Samples can be combined to determine whethether an individual sample exceeds a specified limit as long as thithe action limit is relatively high compared with the actuhmal detection limit and the average sample concentration. DeDe-pending on the difficulty and probability of having t to resample, it may be desirable to retain a split of the discretete samples for possible analysis depending on the analyticsical results from the composite sample.

FIG. 1 Example of Compositing Across a Site

FIG. 2 Example of Within Cell Compositing

6.8 *Example 3*—One hundred drums are to be examined to determine whether the concentration of PCBs exceeds 50 mg/kg. Assume the detection limit is 5 mg/kg and most drums have non-detectable levels. Compositing samples from ten drums for analysis would permit determining that none of the drums in the composite exceed 50 mg/kg as long as the concentration of the composite is <5 mg/kg. If the detected concentration is >5 mg/kg, one or more drums may exceed 50 mg/kg and additional analyses of the individua drums are required to identify any hot drum(s). The max-imum number of samples that can theoretically be com-posited and still detect a hot sample is the limit of concerr divided by the actual detection limit (for example, 50 mg/kq + 5 mg/kg = 10).

6.9 *Example 4*—Assume background levels of dioxin ar non detectable, and the analytical detection limit is 1 μg/kq and the action level is 50 μg/kg. The site is systematicalli gridded (the most efficient sampling design for detecting randomly distributed hot spots) using an appropriate design and cores to a depth of 10 cm are collected. Composit samples are collected since analytical costs for dioxin ar high. In theory, groups of up to 50 samples could b composited and if the resultant concentration were < μg/kg, all samples represented in the composite should b below 50 μg/kg. If the contaminant concentration is > μg/kg, one or more spots may exist that exceed 50 μg/kg i the area covered by the composite sample although th precise location and areal extent would not be know without further sampling and analyses. Compositing fewe samples would probably be more practical, however.

6.9.1 The relative efficiency of compositing individu samples to detect a hot spot depends on the probability of "hot" discrete sample being used to form a composi sample. According to Garner et al. (1), if the probability ca be estimated as low, say 1 %, the optimum number samples to composite is about ten, which would result in cost saving of about 80 % (assuming there is no detecti limit problem). When the probability of collecting a samp from a hot spot rises to 10 %, the optimal number of samp to composite is 4, which results in a 40 % cost savings. By t time the probability of sampling a hot spot rises to 40 there is no cost benefit to compositing. Other resampling a testing schemes are possible and may lead to somewl different cost saving potentials.

7. Limitations of Composite Sampling

7.1 The principal limitations of sample compositing volve the loss of the discrete information contained i single sample and the potential for dilution of the conta nants in a sample with uncontaminated material; howe

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in that case, the dilution factor can be used to estimate the maximum number of samples that can be composited. The following situations may not lend themselves to cost-effective sample compositing:

7.1.1 When the integrity of individual sample values change because of compositing, for example, chemical interaction occurs between constituents in the samples being combined or volatiles are lost during mixing.

7.1.2 Where the composite sample cannot be properly mixed and subsampled or the whole composite sample cannot be analyzed,

7.1.3 When the goal is to detect hotspots and a large proportion of the samples are expected to test positive for an attribute, compositing and retesting schemes may not be cost effective,

7.1.4 When analytical costs are low relative to sampling costs (for example, in situ field portable X-ray fluorescence takes only 30 s with no sample preparation so analytical costs/sample are very low), and

7.1.5 When regulations specify that a grab sample must be collected (usually a composite sample covering a limited area is still preferred from a technical standpoint).

8. Sample Mixing Procedures

8.1 Prior to sample mixing, project-specific instructions should be followed regarding sample collection, which may include removal of extraneous sample materials such as twigs, grass, rocks, etc. If samples are sieved or large materials are removed, it may be necessary to record the mass of materials removed for later estimation of contaminant concentration in the original sample. According to particulate sampling theory (4,5) the following sample masses are adequate to represent the corresponding maximum size particles in the sample with a relative standard deviation of 15 %.

Sample Mass, g	Maximum Particle Size, cm
5	0.170
50	0.37
100	0.46
500	0.79
1000	1.0
5000	1.7

8.1.1 Frequently it is necessary to mix an individual or composite sample and obtain a representative subsample(s) for transport to the analytical laboratory. This occurs when multiple containers of the identical material are desired (for example, separate sample jars for metals, semivolatile organics, etc. are desired) or when the original sample (or composite sample) size is greater than accepted by the laboratory. Even when the original sample volume is acceptable, it may be desirable to thoroughly mix the sample prior to transport to an analytical laboratory. However, some samples that have been well mixed in the field may segregate during shipment to the laboratory.

8.1.2 A laboratory typically collects a 0.5 to 30 g specimen (100 g for some extraction tests) from the sample for analysis. Specimens are frequently collected from the surface material in the container or after minimal mixing. Such procedures are inadequate to obtain a small representative specimen from a 100 to 300 g sample. Special mixing and subsampling procedures are necessary to obtain a representative subsample unless the sample is already homogenous.

Field mixing should be considered essential unless it is known that the sample in the container is homogeneous or it is known that the laboratory will homogenize the sample and collect a representative specimen. To help ensure that an unbiased and precise specimen is collected, the analytical laboratory should be provided instructions (preferably with the sample shipment) on homogenizing and obtaining a specimen for analysis. Few laboratories follow good sample homogenizing and specimen collection practices. To meet both sampling and analytical objectives, field and analytical personnel, and the end-user of the data must be aware of the laboratories standard practices for handling, mixing, and obtaining a specimen or specify such practices with the sample shipment.

8.1.3 To avoid subsampling it may be possible to collect a small sample (or composite samples) directly into the sample container that is delivered to the laboratory (Caution: small sample sizes may result in bias by excluding large particles). While no field mixing and subsampling is needed as long as the laboratory homogenizes the sample, it may be advisable to mix such samples anyway (see 8.1.2).

8.1.4 Soil, sediment, sludge and waste samples collected for purgeable/volatile organic compounds' analyses should *not* be mixed and subsampled using procedures described in this guide but other specialized procedures such as combining samples directly into methanol (see Practice D 4547) may be appropriate.

8.1.5 A significant problem with analyzing very small samples is that the smaller the volume of sample actually extracted or analyzed, the less representative that sample may be unless thoroughly mixed/homogenized and subsampled. Therefore, sample compositing without thorough mixing can nullify the potential benefits of compositing.

8.1.6 Methods that may be applicable to field mixing, depending on the matrix, include hand mixing in a pan, sieving, particle size reduction, kneading, etc. For highly heterogeneous waste such as municipal refuse, field comminution (grinding) may be needed. Some of these methods may be inappropriate if trace levels of contamination are a primary concern. The use of disposable equipment for mixing should be considered to minimize field decontamination problems. Field personnel should use care to ensure that samples do not become contaminated during the sampling, mixing and subsampling process.

8.1.7 Once a sample has been collected, it may have to be split into separate containers for different analyses. A true split of soil, sediment, or sludge samples may be difficult to accomplish under field conditions.

8.1.8 The following are some common methods for mixing soils, sludges, etc. While it is not always possible to determine that a sample is adequately mixed, following standard procedures and observing sample texture, color, and particle distribution are practical methods. While some materials cannot be homogenized, following the subsampling procedures in Section 9 will help ensure that a representative subsample is collected. Under certain conditions, some of the procedures that follow are applicable when trace level contaminants are of concern.

8.1.8.1 *Pan Mixing/Quartering*—One common method of mixing is referred to as quartering. Place the material in a glass or stainless steel sample pan and divide into quarters.

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Mix each quarter separately, then mix all quarters into the center of the pan. Repeat this procedure several times untiltil the sample is adequately mixed (usually a minimum of threese repetitions). If round bowls are used for sample mixing, g. ~terate mixing is achieved by stirring the material in a a circular fashion and occasionally turning the material over. :.

8.1.8.2 *Mixing Square*—Combine samples through a a non-contaminating screen into an appropriate clean mixingig container. Mix in the container and pour onto a 1 metrere square of non-contaminating material such as plastic forχr metals analyses or polytetrafluoroethylene for organics. Rollill the sample backward and forward on the sheet whilele alternately lifting and releasing opposite side corners of theκ sheet. This is appropriate for flowable granular materials (6).). If polytetrafluoroethylene sheeting is used, this procedurere could be acceptable for trace level contaminants.

8.1.8.3 *Kneading*—Place the sample in a non-contami-}- nating bag and knead as in bread making to mix the sample. e. This may be appropriate for viscous or clay-like materials. IfIf a non-contaminating bag is used, this approach would beκ acceptable for trace level contaminants.

8.1.8.4 *Sieving and Mixing*—If a laboratory requires a a small specimen (1 to 30 g) or if less than a specific particlele size is required, disruption of aggregated particles or sieving, }. or both, followed by mixing may be needed. Sieving allows rs only those particles below a desired size to pass through the ιe sieve into a mixing pan for subsequent mixing and d subsampling into containers. Sieving works best with rela-t- tively dry granular materials. Sieving and the exclusion of if large particles can result in very biased results and should d only be conducted when designed into a sampling plan.

8.1.8.5 *Particle Size Reduction*—When particle size re- ⊢ duction is appropriate and trace contaminants are of con- ⊢ cern, non-contaminating materials compatible with objec- ⊢ tives should be used (for example, glass, ceramic, stainless з steel). Other materials may be acceptable if trace levels of if contaminants are not a concern. The reduction method can n be as simple as using a hammer to break apart large pieces з into smaller pieces that are either acceptable to the labora- .-

tory or that can pass through a sieve. This method of reduction creates a great deal of fine material which may or may not be included in the sample container, and could introduce bias. More complex reducers, such as ball mills, ceramic plate grinders, etc, are available, but usually require relatively dry samples and thorough decontamination to avoid cross contamination. Such a process may be more appropriately conducted in a laboratory.

8.1.9 With thorough decontamination (see Practice D 5088) of the particle size reducer, sieve and the mixing pan, these procedures could be acceptable for trace level contaminants.

8.1.10 *Other Mixing Equipment*—Riffle splitters, coning and quartering, etc., involve equipment and materials that are difficult to decontaminate, and awkward to use on a routine basis for waste management sampling. Since these procedures are not routinely used, the devices are not considered in this guide. However, procedures for coning and quartering, and the use of riffle splitters are described in Practice C 702 and could be modified for subsampling contaminated media.

9. Field Subsampling Procedures

9.1 If mixing procedures could ensure a truly homogenous sample, subsampling would be simple. Mixing of various particle sizes may, however, cause the particles to segregate according to size, and improper subsampling could introduce bias. Since homogeneity is frequently not achieved, appropriate subsampling procedures should be used by field personnel to provide representative sul samples. The procedures that follow are appropriate for collecting a representative sample from a larger sample. As noted previously, riffle splitters and coning and quartering procedures can also be used for subsampling as well as mixing (see Practice C 702).

9.1.1 *Rectangular Scoop*—As the final step of mixing, the material is arranged in a pile along the long axis of the rectangular pan. A flat bottomed scoop with vertical sides is moved across the entire width of the short axis of the pile to collect a swath of sample (Fig. 3). Multiple evenly-spaced
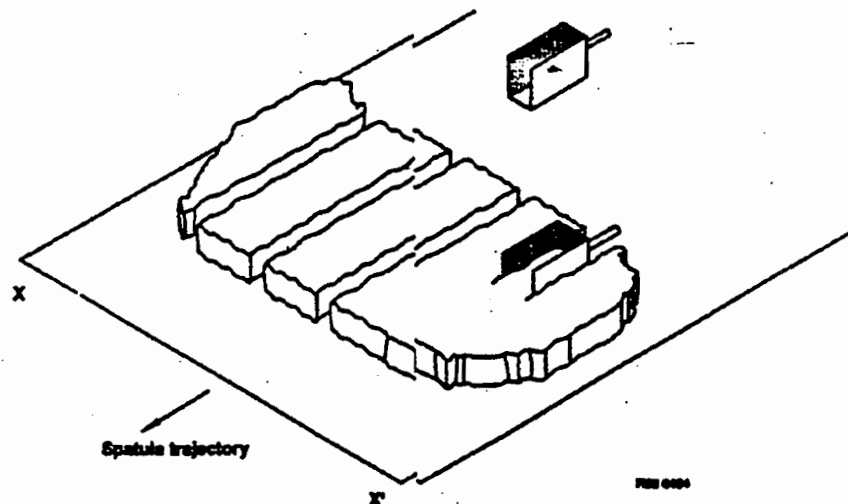

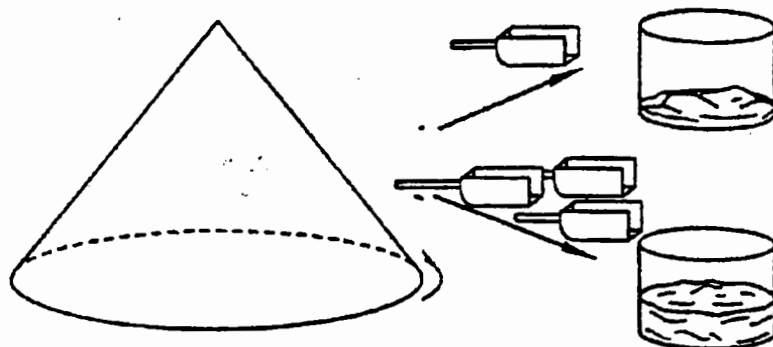FIG. 3 Rectangular Scoop as Used to Collect Swaths for Subsample

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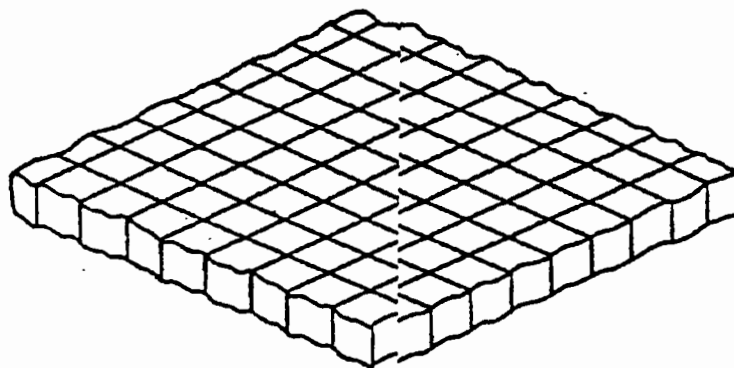FIG. 4   Alternate Scoop & Subsampling Technique

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FIG. 5   Slab Cake Subsbeampling Technique

swaths are collected until the subsample container is full. Multiple containers are filled by rearranging the remaining material and collecting swaths as just described.

9.1.2 *Alternate Scoop*—The volume of material required for filling sample containers is compared to the volume of the mixed sample. Scoops of mixed material are placed in the sample container(s) or are discarded, that is, three scoops are discarded for every scoop saved when collecting a 25 % subsample (Fig. 4). Care should be taken that each scoop of material is of the same size and is collected in a consistent manner to minimize bias (5).

9.1.3 *Slab-cake*—The cohesive or clay-like materials as

discussed in 8.1.8.3 on kneading. The sample can be flattened, cut into cubes (Fig. 5) and the cubes randomly or systematically combined into subsample(s) (5). The subsample should be re-kneaded before shipment to the laboratory unless it can be ensured that the laboratory will homogenize the subsample before collecting a specimen.

10. Keywords

10.1 composite; compositing; hot spot; particle size reduction; sample; sampling; subsample; subsampling

6 6

REFERENCES

(1) Garner et al., "Composite Sampling for Environmental Monitoring in Principals of Environmental Sampling," in *Principles of Environmental Sampling*, American Chemical Society (ACS), Keith, L. L., ed., 1988, pp. 363–374.

(2) Mack, G. A., and Robinson, P. E., "Use of Composited Samples to Increase the Precision and Probability of Detection of Toxic Chemicals," in *Environmental Applications of Chemometrics*, ACS Symposium Series 292, ACS, Washington, DC, 1985, pp. 174–18183.

(3) Rajagopal, R., and Williams, L. R., "Economics of Sample Compositing as a Screening Tool in Ground Water Monitoring," *Ground Water Monitoring Review*, 1989, pp. 186–192.

(4) Ramsey, C. A., Ketterer, M. E., and Lowery, J. H., "Application of Gy's Sampling Theory to the sampling of Solid Waste materials," in *Proceedings of the EPA Fifth Annual Waste Testing and Quality Assurance Symposium*, 1989, p. II-494.

(5) Pitard, F. F., "Pierre Gy's Sampling Theory and Practice," *Sampling Correctness and Sampling Practice*, Volume II, CRC Press, Boca Raton, FL, 1989, p. 247.

(6) U.S. Environmental Protection Agency (EPA), *Description and Sampling of Contaminated Soils, A Field Pocket Guide*, EPA/625/12-91/002, 1991.

7

APPENDIX O
List of Project Participants

O-1
MSD Participants

Mike Heitz
On-Site Coordinator
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1600 Gest Street
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(513) 244-5137
(513) 244-5145 (fax)

O-2
USEPA Participants

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U.S. Environmental Protection Agency
Emissions Standards Division (ESD)
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crumpler.gene@epa.gov

C. E. (Gene) Riley
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Office of Air Quality Planning and Standards (OAQPS)
U.S. Environmental Protection Agency
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O-3
Battelle Participants

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O-4
ETS Participants

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O-5
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O-6
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O-7
Quanterra Environmental Services
Participants

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APPENDIX P

Post Test Summary

P-1
Post Test Summary Report

Internal Distribution
AS Wisbith
KB Riggs
J Ferg
RMO
Project Files

	Name	Initials	Date
Originator	AS Wisbith	Draft *ASW*	08/24/99
Approved	KB Riggs	Draft	08/24/99

Sent Via: 1^{st} *Class Mail*

August 25, 1999

Mr. C.E. Riley
U.S. Environmental Protection Agency
Emission Measurement Center
MD-19
Research Triangle Park, North Carolina 27711
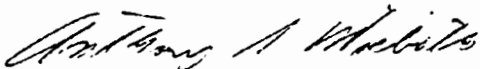
Dear Gene:

Contract No. 68-D-99-009
Work Assignment WA 1-05

As per your request, we are submitting the attached post test summary report for the above work assignment. This report meets the requirements of Section 7.3 of the Site-Specific Test Plan for this task. Also attached are the field logs for the same test.

If you have any questions regarding this report, please call me at (614) 424-5481 to discuss.

Sincerely,

Anthony S. Wisbith
WA 1-05 Work Assignment Leader
Battelle

ASW:llg

cc: Ms. Kathy Weant (letter only)

POST-TEST SUMMARY REPORT

Sewage Sludge Incinerator Test Program
Work Assignment WA 1-05
EPA Contract No. 68-D-99-009

August 25, 1999

A Site-Specific Test Plan (SSTP) was prepared for the test program performed on the sewage sludge incinerator located at the Metropolitan Sewer District in Cincinnati, Ohio. The field test was conducted on July 18-23, 1999. Deviations from the SSTP were expected to occur, due to unforeseen problems with the test location or with the actual sampling. A section of the SSTP (Section 7.3) discussed the submittal of a test deviation letter report to detail all deviations from the SSTP. There were a total of five (5) deviations from the SSTP. The following details the five deviations from the SSTP which occurred during the field test.

The first deviation from the SSTP occurred on July 19, 1999 at 1100. This deviation involved the audit gases from the facility total hydrocarbon analyzer. Section 6.2.2 of the SSTP stated that a cylinder gas audit (CGA) would be performed on the hydrocarbon analyzer prior to and following the test program, in accordance with the procedures of 40 CFR 60, Appendix F, Section 5.1.2. The procedure requires the total hydrocarbon analyzer to be challenged with two audit gases of known concentrations, a high calibration gas of 150 to 180 ppm and a low calibration gas of 60 to 90 ppm would be used to challenge the analyzer.

The deviation from the SSTP involved the high calibration gas. Due to availability, a high gas of 124.6 ppm was used to challenge the total hydrocarbon analyzer, which does not fall within the stated range. This deviation was approved by the EPA WAM, C.E. (Gene) Riley of USEPA's Office of Air Quality Planning and Standards (OAQPS) since
the total hydrocarbon analyzer used the low end of their electronic span, making the lower gas acceptable.

The second deviation from the SSTP occurred on July 19, 1999 at 1530. This deviation involved the span of the carbon monoxide (CO) continuous analyzer. Section 5.1.1.6 of the SSTP states that the range of the CO analyzer would be 0-3000 ppm_{dv}.

Mike Heitz of the Cincinnati MSD stated that spikes of CO to over 10,000 ppm are possible during normal operation. ETS had calibration gases onsite which could raise the instrumental span to 6000 ppm. A calibration gas of 9556 ppm was shipped overnight from the ETS office in Roanoke, Virginia to the Cincinnati MSD to allow for linearity determinations of up to 10,000 ppm, if the 6000 span was exceeded during

testing. The CO analyzer was calibrated to a span of 6000 ppm for all subsequent sampling, and the 6000 span was never exceeded. '

The third deviation from the SSTP occurred on July 20, 1999 at 0830. The deviation involved the proof blanking procedures. Preliminary flowrate provided by the facility indicated that the sampling train should be equipped with a nozzle with a internal diameter of 0.218 inches. Proof Blank #1 was performed on the glassware to be used in the sampling, including this nozzle. On the morning of the initial day of sampling, preliminary flowrate measurements indicated that the nozzle diameter needed to be 0.250 inches to maintain isokinetics and achieve the desired sampling volumes during the preset 360 sampling duration. Since all nozzles were cleaned identically and concurrently, and since the nozzles were similar in size, the WAM accepted the Proof Blank #1 samples were submitted with the incorrect nozzle.

The fourth deviation from the SSTP occurred on July 20, 1999 at 0830. The deviation involved the possible detection of gas stratification in the exhaust stack. Section 5.1.1.1 of the SSTP stated that sampling for carbon monoxide, oxygen, and carbon dioxide would be conducted at a single point in the centroidal area of the duct. A gas stratification determination was performed on July 19, 1999. The single CEM system determination indicated that gas stratification was possible in the exhaust stack. The stratification was not proven since the single CEM system does not allow for comparisons to a stationary CEM system which would correct for process instability. Since the gas stratification determination proved to be inconclusive, a decision was made to traverse the CEM sampling probe using the same traverse points as the modified method 5 sampling train incorporated as detailed in Section 5.1.1.1 of the SSTP.

The fifth and final deviation from the SSTP occurred on July 20, 1999 at 1230. This deviation involved the failure to meet leak checking criteria as stated in the SSTP. Section 5.1.1.5 of the SSTP stated that leak checks will be performed prior to initiating sampling, during each port change, and at the conclusion of each test run. The leak checks would be considered acceptable if a leak rate of less than 0.02 ft^3/min is observed at the highest vacuum recorded during the sampling run. If the leak check is not acceptable, the WAM will be notified, and a decision whether to keep the sampling run, continue the run, or repeat the run will be made.

At the port change of the first sampling run, the leak check was not deemed to be acceptable. The WAM was notified, and after discussion, it was determined that the sampling run should be invalidated. Sampling was discontinued, the sampling train was recovered using the stated procedures in the SSTP, and a total of four sampling runs were performed, so that three valid sampling runs were available for laboratory analyses.

The discussion above details all deviations from the SSTP submitted for review prior to the test program. All other methodology and QA/QC procedures were performed as detailed in the SSTP.

ETS, Inc.
FIELD LOG

Client: EPA/Battelle/Cincinnati MSD

ETS Contract No.: 99-487-W2

Client Contact: Gene Riley/Tony Wiseman

Acknowledgement: _____

Date	Task	Start Time	End Time	Hours	On Scope?	Reason
7/18/99	Meet at ETS, Check Equipment	10:00	11:00	1.0	Y	
"	Travel to Cincinnati (Pick up Chevy Dav @ 12:00 1/2-Hour for Dinner)	11:00	20:30	9.5	Y	
7/19/99	Arrive on Site Check in / Safety Meeting	07:30	08:30	1.0	Y	
	WTU/CBD/FEC Setup Sampling AAH Tours Facility / Lab	08:30	10:00	1.5	Y	
	Delay - No Power to Truck Cannot Access Lab	10:00	11:00	1.0	N	
	WTU/CBD/FEC Continue Setup AAH Performs CGA (11:00-11:30) and Set Up / Access Lab	11:00	14:30	3.5	Y	

ETS, Inc.
FIELD LOG

Client: EPA / BATTELLE / CINCINNATI MSD

ETS Contract No.: 99-487-W2

Client Contact: GREG RILEY / TERRY WUSATH

Acknowledgement: _____

Date	Task	Start Time	End Time	Hours	On Scope?	Reason
7/19/99	PRELIMINARY FLOW / MOISTURE AND RESPONSE TIME CHECKS	14:30	15:30	1.0	Y	
	STRATIFICATION CHECK (WTH/FPS/SBD) REVERT DIAMOS (AAH) FPC/SBD LEAVE SITE @ 17:30	15:30	17:00	1.5	Y	
	COMPLETE LAB SETUP, PROP BLANK #1, PREPARE RUN TRAIN AAH/WTH LEAVE SITE @ 20:00	17:00	20:00	3.0	Y	
7/20/99	ARRIVE ON SITE, PRETEST PREPARATION	07:00	09:30	2.5	Y	
	MSD-MM5-R1	09:30	12:30	3.0	N	FAILED LEAK CHECK - RUN VOID
	FAILED LEAK CHECK, RECOVER/ RECHARGE TRAIN, PREPARE FOR MSD-MM5-R2	12:30	15:00	2.5	N	" " FPC/CBD — 1-HOUR LUNCH

ETS, Inc.
FIELD LOG

Client: ETA/Battelle Cincinnati MSD

ETS Contract No. 99-487-W2

Client Contact: Gene Riley / Tony Wadith

Acknowledgement: _____

Date	Task	Start Time	End Time	Hours	On Scope?	Reason
7/20/99	MSD-MM5-R2	15:00	21:30	6.5	Y	
7/20/99	LEAK CHECK, SECURE EQUIPMENT FFC AND CBD LEAVE SITE AT 22:00	21:30	22:00	0.5	Y	
7/20/99	RECOVER MSD-MM5-R2 AAH/LTU LEAVE AT 23:30	22:00	23:30	1.5	Y	
7/21/99	SETUP AND RECOVER FIELD PROOF BLANK #2 PREP GLASSWARE FOR MSD-MM5-R3, FFC AND SBD ARRIVE @ 08:30	07:00	09:00	2.0	Y	
	FIELD BLANK #1 AND RECOVERY	1015	1430	4.25	Y	
7/21/99	EQUIPMENT SETUP AND LEAK CHECK	09:00	10:15	1.25	Y	
7/21/99	MSD-MM5-R3	1015	16:35	6.25	Y	

ETS, Inc.
FIELD LOG

Client: EPA /Battelle /Cincinnati MSD

Client Contact: Gene Riley /Tony Wroth

ETS Contract No.: 99-487-WZ

Acknowledgement:

Date	Task	Start Time	End Time	Hours	On Scope?	Reason
7/21/99	LEAK CHECK, SECURE EQUIPMENT, FPC/CBD LEAVE @ 17:15	16:35	17:15	0.75	Y	
	RECOVER MSD-MM5-R3 RELINQUISH SAMPLES AH/LZU LEAVE @ 19:15	17:15	19:15	2.0	Y	
7/22/99	ARRIVE ON SITE, PRETEST PREP. — ETS METHOD 3A/10 QAD AUDIT (07:10-07:40) —	06:30	08:15	1.75	Y	
	MSD-MM5-R4	08:15	14:35	6.25	Y	
	LEAK CHECK, BEGIN DISMANTLING MSD THC MONITOR CGA (14:30 - 15:13) METAL BOX POST-TEST AUDIT (15:00 - 16:10) (FPC/CBD LEAVE @ 18:30)	14:35	16:15	1.75	Y	
	DISMANTLE, SAMPLE RECOVERY (FPC/CBD LEAVE @ 18:30)	16:15	19:00	2.75	Y	
7/23/99	TRANSFER SAMPLES /RETURN TO ROANOKE	07:30	16:00	8.5	Y	

	TEST LOG				
	Metropolitan Sewer District				
	Sewage Sludge Incinerator				
	Cincinnati, Ohio				

Test Location	Activity	Test Parameter(s)	Date	Start Time	End Time
MSD CEMS	Pre-Test Cylinder Gas Audit	Total Hydrocarbons		1100	1130
Outlet Stack Inlet	Cyclonic Flow Check/Preliminary Flowrate	Flowrate		1430	1530
Outlet Stack	ETS RM Response Time	$CO/CO_2/O_2$		1435	1545
Outlet Stack	Stratification Check	$CO/CO_2/O_2$	7/19/99	1540	1630
Sample Recovery Laboratory	Reagent Blanks	CoplanarPCBs Dioxins/Furans PAHs		1530	1700
Sample Recovery Laboratory	Proof Blank #1	CoplanarPCBs Dioxins/Furans PAHs		1700	2000
Stack Outlet	MSD-MM5-R1	CoplanarPCBs Dioxins/Furans PAHs		0930	1230
Stack Outlet	MSD-CEMS-R1	$CO/CO_2/O_2$		0930	1230
Stack Outlet	MSD-MM5-R2	CoplanarPCBs Dioxins/Furans PAHs	7/20/99	1500	2130
Stack Outlet	MSD-CEMS-R2	$CO/CO_2/O_2$		1500	2130

TEST LOG

Metropolitan Sewer District

Sewage Sludge Incinerator

Cincinnati, Ohio

Test Location	Activity	Test Parameter(s)	Date	Start Time	End Time
Sample Recovery Laboratory	Proof Blank #2	CoplanarPCBs Dioxins/Furans PAHs	7/21/99	0700	0900
Stack Outlet	MSD-MM5-R3	CoplanarPCBs Dioxins/Furans PAHs		1015	1635
Stack Outlet	MSD-CEMS-R3	$CO/CO_2/O_2$		1015	1635
Stack Outlet	Field Blank #1	CoplanarPCBs Dioxins/Furans PAHs		1015	1430
ETS Mobile Laboratory	Reference Method CEMS Gas Audit	$CO/CO_2/O_2$	7/22/99	0710	0740
Stack Outlet	MSD-MM5-R4	CoplanarPCBs Dioxins/Furans PAHs		0815	1435
Stack Outlet	MSD-CEMS-R4	$CO/CO_2/O_2$		0815	1435
MSD CEMS	Post-Test Cylinder Gas Audit	Total Hydrocarbons		1430	1515
Stack Outlet	Post-Test Meter Box Audit	Critical Orifice		1500	1610

P-2
QAPP Amendment Records

For Review and Approval   Project No G003635-03 (3190)

	Name	Initials	Date
Originator	K Lesniak	✗	✗/11/99
Concurrence	T Wisbith	A.W	8/11/99
Concurrence			
Approved	KB Riggs	gug	8/11/9A

Sent Via: FedEx, Fax

August 11, 1999

Mr. C. E. Riley
Office of Air Quality Planning and
   Standards (OAQPS)
U.S. Environmental Protection Agency
Emissions Measurement Center
Mail Drop 19
Research Triangle Park, NC 27711

Contract No. 68-D-99-009
Work Assignment WA 1-05

Dear Mr. Riley:

Enclosed please find five Quality Assurance Project Plan (QAPP) Amendment Records for your approval and
signature. Copies of these forms were faxed to you on the above date. Please return these forms after they have
been approved so that I may include them in the final report. Also included are completed copies of the QAPP
Amendment Records from the field for your records.

If you have any questions regarding these forms, please call me at (614) 424-5481 to discuss. Thank you for your
continued assistance.

Sincerely,

Anthony S. Wisbith
WA 1-05 Work Assignment Leader
Battelle

ASW:kl
Enc.

(557)

Quality Assurance Project Plan
Project No.: Sewage Sludge Inciner
Section No.: B2.2
Revision No.: 1.0
Date: 7-19-99
Page No.: 19 ÷ 23

QAPP Change No. 1

QUALITY ASSURANCE PROJECT PLAN AMENDMENT RECORD

QAPP Title/Date: Sewage Sludge Incinerator
Metropolitan Sewer District
Cincinnati, OH
July 16, 99

Change Initiator/Name &Title: Eugen Crumpler
EPA/ESD Program Manager

Agency/Company: USEPA

Description (Statement, Reason, and Amendment)

Change: Add collection of outlet scrubber water samples at the incinerator and venturi scrubber outlet for monitoring of the pH and temperature of exiting water as well as obtaining PCB, D/F, chlorine and total of solids on the outlet venturi scrubber water

Reason for change: After reviewing the actual operation of the venturi scrubber system, Mr. Crumpler believed that the scrubber outlet data would be needed to compare with the inlet scrubber water data. This would provide effluent data for the outlet scrubber water test parameters and the actual operation of the scrubber could be monitored during the emission testing. The venturi scrubber water would be collected during simultaneous with the venturi scrubber water inlet samples. The outlet water samples would also be processed the same as the inlet water samples

(attach additional pages if needed)

Signatures:
Contr. Project Lead Engr. _____ Date 7/22/44
Contr. Project QA Lead _____ Date 7-29-99
EPA WAM _____ Date 7/22/99
EPA QA _____ Date 7/27/99
Initiator (if other than WAM) _____ Date 7/22/99

(SSI)

Quality Assurance Project Plan
Project No.: Sewage Sludge Incinerator
Section No.: B.2 & B.3
Revision No.: 1
Date: 7-19-99
Page No.: 19 → 23 + 25

QAPP Change No. 2

QUALITY ASSURANCE PROJECT PLAN AMENDMENT RECORD

QAPP Title/Date: Sewage Sludge Incinerator
Metropolitan Sewer District
Cincinnati, OH
July 16, 1999

Change Initiator/Name &Title: Clyde F. Riley
EPA Work Assignment Manager

Agency/Company: US EPA

Description (Statement, Reason, and Amendment) (venturi in and out scrubber water & sewage sludge)

Change: Increase the process grab sampling time from one sample every one-half hour to one sample every four. The process grab samples (inlet and outlet scrubber water, and sludge) were being collected by one field technician. The samples had to be collected at different locations in the plant, some of these locations were not adjacent to each other. In addition, the tech had to measure the pH and temp on each of the two scrubber water grab samples. Also the collection equipment and apparatus had to be cleaned between each grab sample collection. It was decided to collect the process samples every four instead of every half hour to provide the technician sufficient time between sample collection to do the required monitoring and QA/QC work. Compositing of the process samples as well as the volumes/weights required for the different analyses remained the same.

(attach additional pages if needed)

Signatures:
Contr. Project Lead Engr. _____ Date 7-22-99
Contr. Project QA Lead _____ Date 7-29-99
EPA WAM _____ Date 7-26-99
EPA QAO _____ Date 7/27/99
Initiator (if other than WAM) _____ Date _____

Quality Assurance Project Plan
Project No.: _SSI_
Section No.: _R4.6_
Revision No.: _1.0_
Date: _7-20-99_
Page No.: _29/30_

QAPP Change No. _3_

QUALITY ASSURANCE PROJECT PLAN AMENDMENT RECORD

QAPP Title/Date: _Sewage Sludge Incinerator_
Metropolitan Sewer District
Cincinnati, OH
July 16, 1999

Change Initiator/Name &Title: _Eugene Crumpler_
EPA ESD Program Manager

Agency/Company: _US EPA_

Description (Statement, Reason, and Amendment)

Change: Add ultimate and proximate analyses measurements
for sewage sludge samples.

Reason for change: Mr. Crumpler, after becoming
familiar with the SSI operation, decided that additional
sludge data were needed to evaluate the thermal
characteristics of the sludge for BTU content, % moisture,
ash, etc. This would require collecting an additional
_sludge composite for each run. Sufficient ___ ____
The grab sludge sampler already provided sufficient
sample volume for this sampling, therefore no additional
collection of sample was needed. These samples will
be stored and processed identical to the other
sludge samples.

(attach additional pages if needed)

Signatures:

Contr. Project Lead Engr.	Date	7-22-99
Contr. Project QA Lead	Date	7-29-99
EPA WAM	Date	7/22/99
EPA QAO	Date	7/27/99
Initiator (if other than WAM)	Date	7/22/99

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Quality Assurance Project Plan
Project No.: _5.5 Z_
Section No.: _B3. 1_
Revision No.: _1.0_
Date: _7-23-99_
Page No.: _18 / 19_

QAPP Change No. _4_

QUALITY ASSURANCE PROJECT PLAN AMENDMENT RECORD

QAPP Title/Date: _Sewage Sludge Incinerator_
Metropolitan Sewer District
Cincinnati, OH
July 20, 1955

Change Initiator/Name &Title: _Clyde E. Riley_
EPA Work Assignment Manager

Agency/Company: _U S E P A_

Description (Statement, Reason, and Amendment)

Change: Voiding a Flue gas sample (Run 1).
7-20-99. The first stack MM-5 sample was collected
09:30 - 12:30. The train was leaded-checked after completion
of the 1st port. A leak of 0.06 DSCF/M was measured
@ 15" Hg.
It was decided to void the 1st run and restart the
run with a clean train.

The W&M directed Battelle to recover the Run 1
sample just in case, a replacement run was not
collected. The Run 1 sample fractions are to be
archived until a replacement run can be collected
at which time the Run 1 fractions can be disposed.
The Run 1 samples were sent to Battelle Columbus
for storage. After collection of 3 good stack MM-5
runs, the Battelle W&M is to instruct that the Run 1
sample be disposed of.

(attach additional pages if needed)

Signatures:
Contr. Project Lead Engr. _[signature]_ Date _7-22-99_
Contr. Project QA Lead _[signature]_ Date _7-23-99_
EPA WAM _[signature]_ Date _7-22-99_
EPA QA _[signature]_ Date _7/27/99_
Initiator (if other than WAM) _____ Date _____

Run 1 moisture — 4.5 %
  2   "   — 4.6 %
  3   "   — 4.2 % P-16

Quality Assurance Project Plan
Project No.: _SS I_
Section No.: _B 5. 2_
Revision No.: _1.0_
Date: _7-21-99_
Page No.: _48_

QAPP Change No. _5_

QUALITY ASSURANCE PROJECT PLAN AMENDMENT RECORD

QAPP Title/Date: _Sewage Sludge Incinerator_
Metropolitan Sewer District
Cincinnati, OH
July 21, 1999

Change Initiator/Name &Title: _Clyde E. Riley_
EPA Work Assignment Mgr.

Agency/Company: _US EPA_

Description (Statement, Reason, and Amendment) _-3 filter (set) toluene/methylene chloride (2)_
-3 filter (set) toluene/methylene chloride (NZ 2)

Change: _Additional of Two QC Evaluation Samples._
To overcome anticipated problems with the filter
glass filter (full) cleaning, Battelle made some
last - minute changes to the filter cleaning
procedures. This was done at the request of the
EPA WAM

Reason for Change: The organic train will be collecting
samples for 3 different organic species (PAH, PCB and
DF). No evaluation work were done to determine the
best procedure for cleaning the filters. Battelle suggested
heating the filter in a oven (2400°C), however, EPA.
specified that the filter had to be cleaned using toluene
and Possible methylene chloride. Battelle believes that if
the filter is cleaned first with toluene/methylene chloride
and then placed in the oven, that PAHs may be generated.
These QC's are needed to justify the decision made
for cleaning the field filter.

(attach additional pages if needed)

Signatures:

Contr. Project Lead Engr. _[signature]_ Date _7-22-99_
Contr. Project QA Lead _[signature]_ Date _7-29-99_
EPA WAM _Cindy E. Riley_ Date _7-22-99_
EPA QA _[signature]_ Date _7/27/99_
Initiator (if other than WAM) _____ Date _____

Quality Assurance Project Plan
Project No.: _S S E_
Section No.: _B 2.0_
Revision No.: _1.0_
Date: _7-19-99_
Page No.: _22_

QAPP Change No. _6_

QUALITY ASSURANCE PROJECT PLAN AMENDMENT RECORD

QAPP Title/Date: _Sewage Sludge Incinerator_
Metropolitan Sewer District
Cincinnati, OH
July 15, 1999

Change Initiator/Name &Title: _Clyde E. Riley_
EPA Work Assignment Manager
Agency/Company: _U S EPA_

Description (Statement, Reason, and Amendment)

Change: Increase CO instrument gas span from 3000 ppm to 6000 ppm.

Reason: Plant staff stated that the SSI CO could range between 5,000 ppm and 10,000 ppm. Also CO spikes were sometimes seen that extended beyond the 10,000 limits. The WAM discussed the options with the EPA Program Manager (Requester) and with the CEM-CO operator, and the Battelle Project Lead. The WAM decided that the 6000 range would probably be the best range to to meet the measurement criteria for CO (5,000 & 10,000 ppm, possibly > 10,000 spikes and if the CO was in the 50,000 to 5,000 range, then still reliable. The CEM operator did said that 3000 range provided for a 60 ppm error limit which the 6000 range provided for a 120 ppm error... however, he stated that this produced was @ 15 ppm. (see attached Log sheet 7-19-99)   (attach additional pages if needed) see attached sheet

Signatures:

Contr. Project Lead Engr.	_(signature)_	Date	_7-22-99_
Contr. Project QA Lead	_(signature)_	Date	_7-29-99_
EPA WAM	_(signature)_	Date	_7-22-99_
EPA QA	_(signature)_	Date	_7/27/99_
Initiator (if other than WAM)		Date	

7-22-99 - Runs 1, 2, and 3 have been completed and the CO has ranged between 1,000 and 6,000 ppm for all periods, without spikes. WAM decided to leave CO span range @ 6,000 ppm. This will produce data that has all the same QA/QC

Battelle (EPA - Cincinnati MF)

ETS No. 99-487-WZ
NON-CONFORMANCE LOG

GASP chem 6

DATE | TIME

7/19/99 .. 11:00 — AH~~ET~~ AUDIT ~~GASES~~ GAS FOR MID-POINT

CALIBRATION/~~GASES~~ gas DOES NOT CONFORM TO 40CFRL60,

APPENDIX F. SHOULD HAVE 150-180 ppm,

HAVE 129.60 129.6 APPROVED BY C.E.RILEY C.E.R

Low

MONITORS USE LOW END OF SPAN, AND

Lower

~~LOWER~~ GASES ARE ACCEPTABLE

→ scale criteria for QA

7/19/99 .. 1530 DISCUSSION CONCERNING CO SPAN. TEST.

PLAN SPECIFIES 3000 ppm SPAN. MIKE HERTZ

2000 4000

bias error 150 300 OF CINCINNATI MSD CLAIMS SPIKES TO 10,000 ppm

~~span~~ error 60 120 ARE POSSIBLE ETS BOUGHT 6000 ppm CO -

~~drift~~ error 90 180 HAD 9556 ppm SHIPPED IN TO ARRIVE 7/20 am.

ON 7/20 CALIBRATED TO 6000 ppm SPAN

AND HAVE 9556 ppm AVAILABLE FOR

LINEARITY IF 6000 ppm SPAN IS EXCEEDED

7/20/99 0830 MISCALCULATED NOZZLE SIZE. DID PROOF BLANK

WITH 0.218 in NOZZLE. RINSED 0.254 in NOZZLE

AND REPLACED.

_C.E.R_ 7/20/99
AA HERTZ, ETS

C.E. Riley 7/20/99
C.E. RILEY, EPA

SADWRU7-29-99 P-19

Quality Assurance Project Plan
Project No.: _S S T_
Section No.: _B 2. 0_
Revision No.: _1 2_
Date: _7-19-99_
Page No.: _2 2_

QAPP Change No. _7_

QUALITY ASSURANCE PROJECT PLAN AMENDMENT RECORD

QAPP Title/Date: _Sewage Sludge Incinerator_
Metropolitan Sewer District
Cincinnati, OH
July 19, 1997

Change Initiator/Name &Title: _Clyde F. Riley_
EPA WAM

Agency/Company: _US EPA_

Description (Statement, Reason, and Amendment)
Conducted stratification test on stack flow - changed
CEM gas (CO, D, CO,) procedure from being collected
at a single point to being collected at multi-traverse
points.
Reason - Stratification test provided no conclusive
data as to whether gas stream was stratified. WAM
discussed concerns problem w/ Peter Westlin and it was
decided to test at 24 traverse points that were being
used for the MM-5 train. This would provide data
that were representative of the entire stack flow and not
at just one single point. This would produce representative
data if the stack gas were or were/not stratified
(See attached sheet 7-20-99)

(attach additional pages if needed)

Signatures:

Contr. Project Lead Engr.	Date	_1-22-77_
Contr. Project QA Lead	Date	_7-29-99_
EPA WAM _Clyde E. Riley_	Date	_7-22-99_
EPA QAO	Date	_7/37/99_
Initiator (if other than WAM)	Date	

Battelle / EPA — Cincinnati MSD
ETS No. 99-487-WZ
NON-CONFORMANCE LOG

QAPP change 7

DATE	TIME	
7/20/99	08:30	Following the gas stratification check, the DFA were inconclusive as to whether the gas was stratified or the values changed over time due to process fluctuations. It was decided to traverse the method 3A/10 probe at the same time, using the same points (in the other port) as the modified method 5 train
7/20/99	12:30	The train from run 1 failed to leak check at the port change — it was determined that the leak was probably at the top of the XAD trap. The run was voided. The samples were recovered and transferred to Battelle

A.A. Hertz ETZ   7/21/99

C.E. Riley, EPA   7-21-99

P-21

Quality Assurance Project Plan
Project No.: _SS 2_
Section No.: _Appendix D-2-2_
Revision No.: _0.0_
Date: _new 7-16-99 CE 1_
Page No.: _47 - CEA_
QAPP Change No. _8_

QUALITY ASSURANCE PROJECT PLAN AMENDMENT RECORD

QAPP Title/Date: _Sewage Sludge Incinerator Metropolitan Sewer District Cincinnati, Ohio_

Change Initiator/Name & Title: _Karen Lesniak, Research Scientist_

Agency/Company: _Battelle Memorial Institute_

Description (Statement, Reason, and Amendment):

QAPP 8 47. CEA

PCB tie method changes: ① The PAR spike levels in table 3 have been doubled; ② All project specific action (e.g. "discuss with Battelle WAL" or "report to EPA WAM") have been deleted from method; and ③ information on how to calculate the percent recovery of the clean-up standard was added to section 12.2.3 page 41, Appendix D-2-2.

(attach additional pages if needed)

Signatures:

Contr. Project Lead Engr. _____ Date _7-28-99_

Contr. Project QA Lead _____ Date _7-26-99_

EPA WAM _Clyde E. Riley_ Date _8-11-99_

EPA QAO _____ Date _____

Initiator (if other than WAM) _Karen Lesniak_ Date _7/26/99_

Quality Assurance Project Plan
Project No.: _Sewage Sludge Inc_
Section No.: _B4.1_
Revision No: _0.0_
Date: _7-16-99_ _CEO_
Page No.: _31_
QAPP Change No.: _9_

QUALITY ASSURANCE PROJECT PLAN AMENDMENT RECORD

QAPP Title/Date: _Sewage Sludge Incinerator Metropolitan Sewer_
District Cincinnati, Ohio

Change Initiator/Name & Title: _Mary Schrock_
Principal Research Scientist

Agency/Company: _Battelle_

Description (Statement, Reason, and Amendment):

QAPP
Section B4.1, p. 31 Method 8290 PCDD and PCDF by High Resolution Gas Chromatography/
CEO _High Resolution Mass Spectrometry_

First paragraph of this section regarding cleanup and analysis
of emission samples should be modified to read: Cleanup and
anal. of emission samples will be conducted according to Method
8290 with the revisions described in Battelle SOP. Analysis of
emission samples will be conducted according to Method 8290
with revisions described in Battelle SOPs and modifications
from Method 23 to accommodate the use of Method 23 PCDD/PCDF
standards for calibration and spiking.

└ SOP0802-02-01

SOP0802-01-01

CSR 8-18-99

Dewbrry man
MES 7/20/99   (attach additional pages if needed)

Signatures:

Contr. Project Lead Engr.	Date	_7-30-99_
Contr. Project QA Lead	Date	_7-29-99_
EPA WAM	Date	_8-20-99_
EPA QAO	Date	_9/9/99_
Initiator (if other than WAM) _Mary Schrock_	Date	_July 28, 1999_

Quality Assurance Project Plan
Project No.: _Sewage Sludge Inc_
Section No.: _B4.1_
Revision No: _0.0_   CEA
Date: _7-16-99_   _8-18-99_
Page No.: _31_

QAPP Change No.: _R 10_

QUALITY ASSURANCE PROJECT PLAN AMENDMENT RECORD

QAPP Title/Date: _Sewage Sludge Incinerator Metropolitan_
Sewer District   Cincinnati, Ohio

Change Initiator/Name & Title: _Mary Schrock_
Principal Research Scientist

Agency/Company: _Battelle_

QAPP
ction B4.1
CEA
_8-18-99_

Description (Statement, Reason, and Amendment):

p. 31   Method 8290 PCDD and PCDF by High Resolution Gas Chromatography/
High Resolution Mass Spectrometry
_   The description in the first paragraph of this section_
describing a single extraction of sludge and water samples
for both PCB and PCDD/PCDF analysis and splitting this
extract for separate cleanup should be revised to reflect
that separate samples will be extracted for PCB and PCDD/PCDF
analyses. Accordingly, an approximate 1-g sludge sample (wet weight)
will be extracted, cleaned, and analyzed, for PCDD/PCDF, according to Method
8290 with revisions described in Battelle SOP. A 1-L scrubber
water sample will be extracted, cleaned, and analyzed for PCDD/PCDF
according to Method 8290 with revisions described in Battelle SOPs.
_   SP0R 02-01-01 / SP0302-02-c_

(attach additional pages if needed) _CEA_
_8-18-99_

Signatures:

Contr. Project Lead Engr.		Date _7-28-99_
Contr. Project QA Lead		Date _7-29-99_
EPA WAM _Clyde E Riley_		Date _8-20-99_
EPA QAO		Date _9/9/99_
Initiator (If other than WAM) _Mary Schrock_		Date _July 28, 1999_

P-3
SSTP Amendment Records

Site Specific Test Plan
Project No.: _SSI_
Section No.: _See SSTP July 16, 99_
Revision No: _O.O_
Date: _f-6-99 7-16-99_
Page No.: _41 - 42 SSTP_

SSTP Change No.: _1_

SITE SPECIFIC TEST PLAN AMENDMENT RECORD

SSTP
~~QAPP~~ Title/Date: _Sewage Sludge Incinerator_
Metropolitan Sewer District _July 16/1999_
Cincinnati

Change Initiator/Name & Title: _MArk Misita_
Res. Tech

Agency/Company: _Battelle_

<u>Description (Statement, Reason, and Amendment):</u>

Flow Charts Figure 5-8 (Page 41) Flow Chart for
Extraction of Front Half of Sample Train and
Figure 5-9 (Page 42) Extraction of Back Half
of sample Train have been changed as indicated.
This Change was incorporated to keep the extraction
consistant with the proposed analytical method
for toxic Polychlorinated Biphenyl Emissions
July 20, 1999
Changed Figures Attached.

Note - Figures 5-8 and 5-9 are located in the Project   _8-12-99_
_   ced._
Site-Specific Test Plan, July 16, 1999, Section 5.2.2.1 pag 41 & 42.

(attach additional pages if needed)

<u>Signatures:</u>

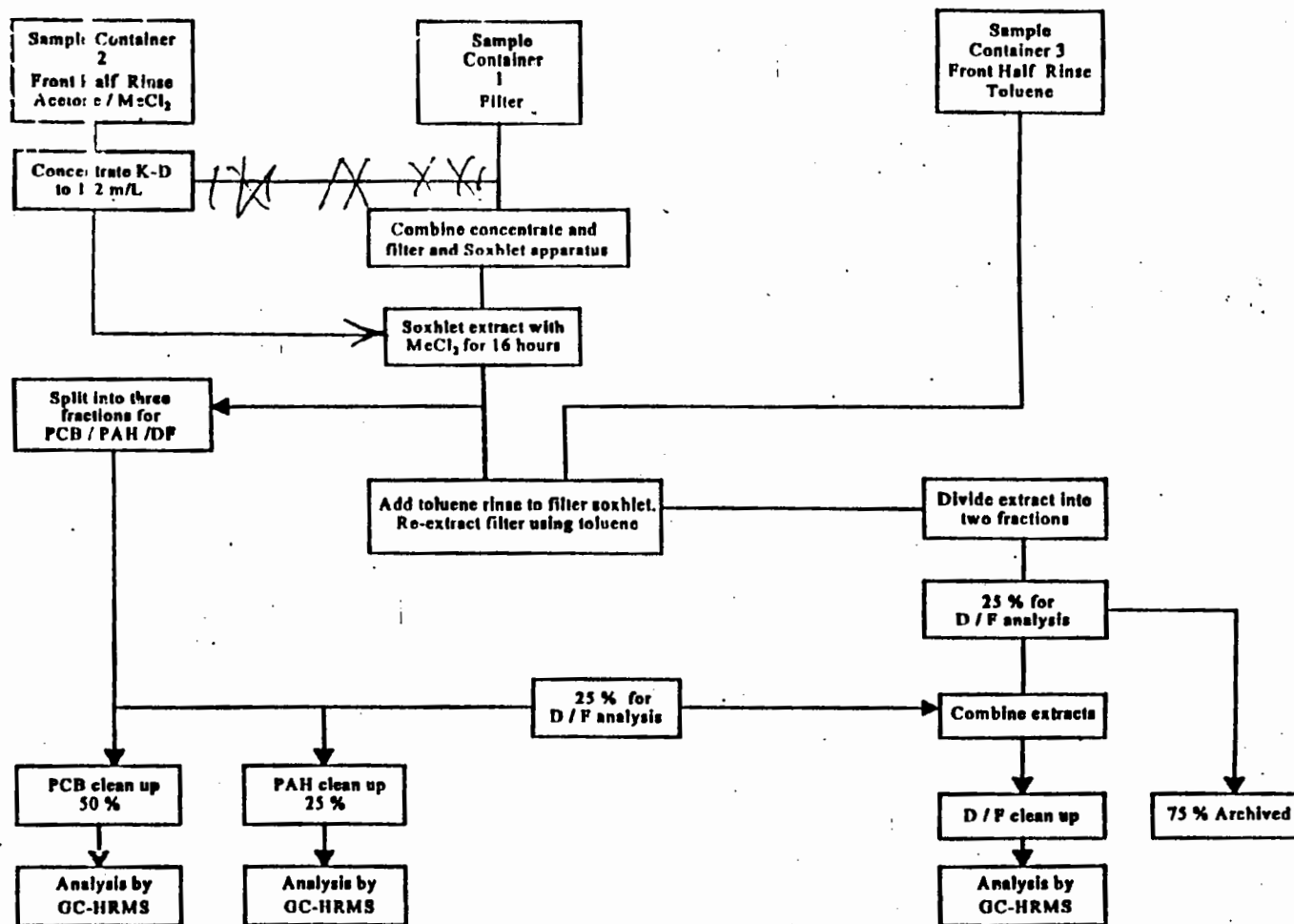|		
Contr. Project Lead Engr. _[signature]_	Date	_8/6/99_
~~Contr. Project QA Lead~~	Date	
EPA WAM _Clyde E. Arley_	Date	_8/12/99_
~~EPA QAO~~	Date	
Initiator (if other than WAM) _[signature]_	Date	_8/5/99_

Figure 5-8. Flow Chart for Extraction of Front Half of Sample Train

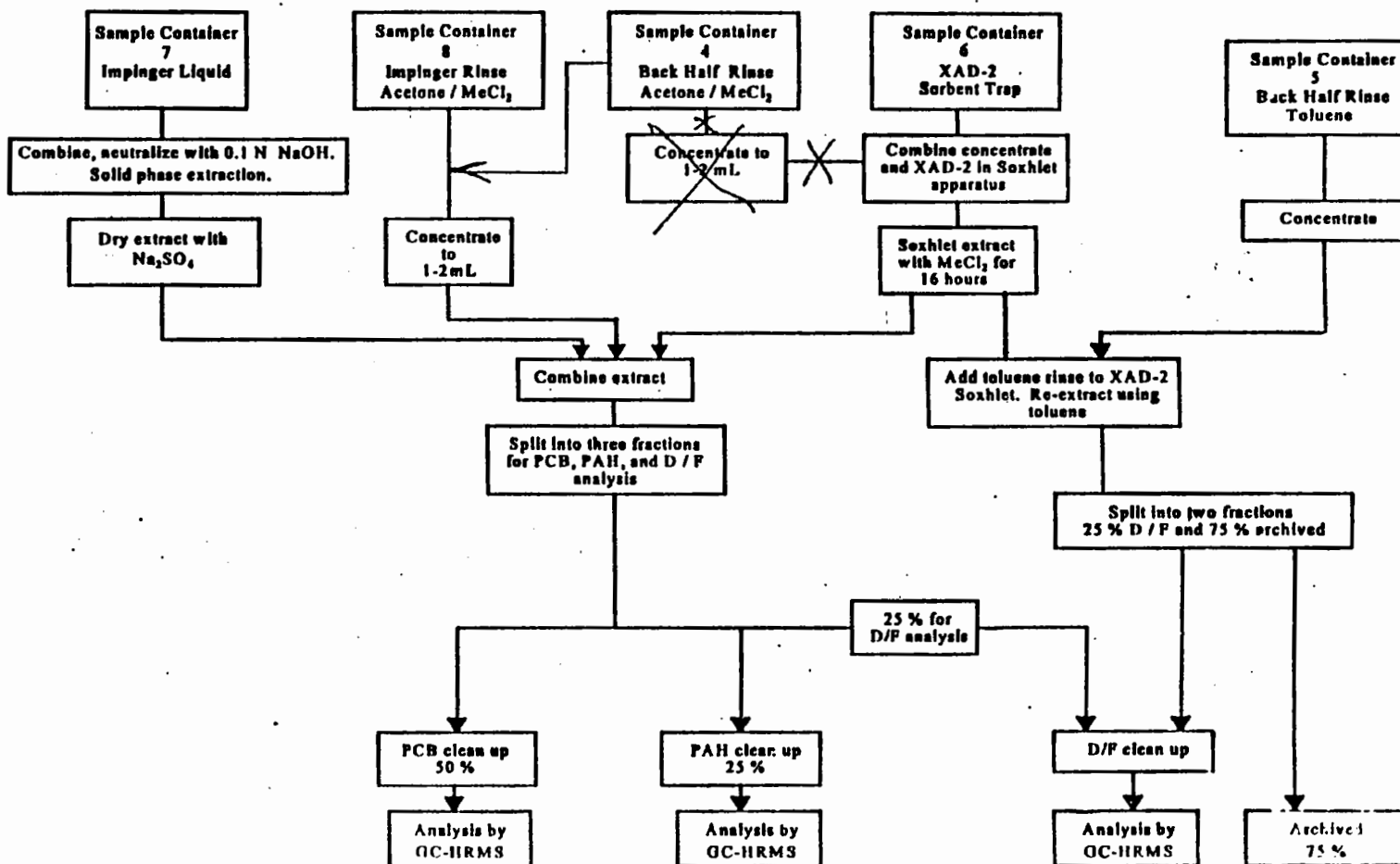**Figure 5-9. Flow Chart for Extraction of Back Half of Sample Train**

P-4
Corrective Action Reports

CORRECTIVE ACTION REPORT
(CAR)

Description of problem: The recommended column for PCB analysis, 50m x 0.25±0.02 mm ID; 0.25 μm film HT-8, produced excessive column bleed causing mass on 8/30/99 lock mass problems.

Action Taken: Section 6.7.1 in both the Scrubber Water and Sewage Sludge methods and section 6.6.3 in the Emissions methods allow the use of other columns not listed in those methods. For the PCB analysis, the 2 columns listed/recommended by method Hole 8 were used. One for initial runs SPB-octyl (Supelco) 30m x.25mm x.25μm, the other for confirmation runs DB-1, JEW 30m x.25 mm x.25 μm

Signatures:

Analyst: Joseph E Tabor Date: 08-25-99

Laboratory Manager/Coordinator: Nancy Schwab Date: 8/25/99

Battelle QA/QC Officer: David R. Davis (acting) Date: 8-26-99

Battelle Work Assignment Leader: Arthur A. Maskin Date: 8-26-99

CORRECTIVE ACTION REPORT
(CAR)

Description of problem: Extraction flow charts from Figure 5-8 of the site-specific test plan and Figure 1 of the PCB Analytical Method are different.

Action Taken: followed Figure 1 of the PCB Analytical Method.

Signatures:

Analyst _____ Date: 8-31-99

Laboratory Manager/Coordinator: _____ Date: 9-1-99

Battelle QA/QC Officer: David B. Davis (acting) Date: 9-1-99

Battelle Work Assignment Leader: _____ Date: 9-7-99

CORRECTIVE ACTION REPORT
(CAR)

Description of problem: Extraction Flow charts from Figure 5-9 of the site-specific Test Plan and Figure 1 of the PCB Analytical method Are different. Also the Sample containers listed in Figure 1 of the PCB Analytical method are Not correct.

Action Taken: The Flow chart from Figure 1 of the PCB Analytical Method was followed using the correct Sample containers.

Signatures:

Analyst: _____ Date: 8·31-99

Laboratory Manager/Coordinator: _____ Date: 9-1-99

Battelle QA/QC Officer: David B. Davis (acting) Date: 9-1-99

Battelle Work Assignment Leader: _____ Date: 9-7-99

CORRECTIVE ACTION REPORT
(CAR)

Description of problem: The dioxin IS ~~used~~ for Method 23 why NCS available to do the Beckground check of the XAD/Fiter.

Action Taken: Dioxin IS for meter 1613 was use as A replacement. This is Jein contained same Anilys of interest.

Signatures:

Analyst: _____ Date: 6-31-99

Laboratory Manager/Coordinator: _____ Date: 9-1-99

Battelle QA/QC Officer: David B. Davis (acting) Date: 9-1-99

Battelle Work Assignment Leader: _____ Date: 9-7-99

CORRECTIVE ACTION REPORT
(CAR)

Description of problem: The Analytical Method For PCBs (A-3) uses a 1mL spike to deliver the Amount of Analytes Required For the pre-fraction spike. 1mL of solvent is to much to be introduced into the XAD resin.

Action Taken: The concentration of the pre-fraction spiking soln was increased at to deliver the same amount of Analytes at 50mL.

Signatures:

Analyst: _____ Date: 8·31·99

Laboratory Manager/Coordinator: Karen Resmie Date: 9-1-99

Battelle QA/QC Officer: David B. Davis (acting) Date: 9-1-99

Battelle Work Assignment Leader: Anthony L. Walker Date: 7-7-99

CORRECTIVE ACTION REPORT
(CAR)

Description of problem: The Internal standards and the surrogate/clean-up standards listed in Table 3 of the PCB Analytical method have spike soln concentrations that do NOT account for the extract being split.

Action Taken: The pre-filed surrogate/internal standard concentration listed on Table 5-3 and Table 5-4 of the site-specific test plan were followed.

Signatures:

Analyst: _____ Date: 8-31-99

Laboratory Manager/Coordinator: _____ Date: 4-1-99

Battelle QA/QC Officer: David B Davis (acting) Date: 9-1-99

Battelle Work Assignment Leader: _____ Date: 9-7-99

P-35

CORRECTIVE ACTION REPORT for PCB sludge samples
(CAR)

Description of problem: After one copper cleanup procedure performed, samples 48190-15 12, 11, 10, 09 and 08 when 48190-99 appeared to need extra clean-up prep performed. 9/28/99

Action Taken: Samples 48190-15-12, 10, 11, 09 and 08 44 48/28/99 carried through a second copper clean-up procedure.

Signatures:
Analyst: _____ Date: 8-31-99

Laboratory Manager/Coordinator: _____ Date: 8-1-99

Battelle QA/QC Officer: David B. Davis (acting) Date: 9-1-99

Battelle Work Assignment Leader: _____ Date: 9-7-99

CORRECTIVE ACTION REPORT
(CAR)

Description of problem: _The H₂O Reagent blanks from the field was SPE extracted, Table 6-1 of the site-specific test plan Has this sample being Archived._

Action Taken: _The Extract was Archived._

Signatures:

Analyst _[signature]_   Date: _8-31-99_

Laboratory Manager/Coordinator: _[signature]_   Date: _9-1-99_

Battelle QA/QC Officer: _David B. Davis (acting)_   Date: _9-1-99_

Battelle Work Assignment Leader: _[signature]_   Date: _9-7-99_

CORRECTIVE ACTION REPORT
(CAR)

Description of problem: The PCB scrubber water contained Fly ash which was not identifiable during visual estimate. This Fly ash prevented sufficient sample throughout the PCB scrubber H2O Analytical method allows a total of three SPE columns to be used which did not allow for sufficient sample throuput.

Action Taken: Ran the following samples through more then 3 SPE columns:

Sample	total # of columns
MSO-WI-R2-211B	4
R3-311B	5
R4-411B	5
MSO-WO-R2-212B	4
R3-312B	4
R4-412B	4

Signatures:
Analyst: _____ Date: 8-31-99
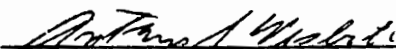
Laboratory Manager/Coordinator: _____ Date: 9-1-99

Battelle QA/QC Officer: David B Davis (acting) Date: 9-1-99

Battelle Work Assignment Leader: _____ Date: 9-2-99

CORRECTIVE ACTION REPORT
(CAR)

Description of problem: The second and third continuing calibrations did not pass the method criteria on the first day of PCB analysis.

Action Taken: An initial calibration curve was analyzed after the third continuing calibration. The three continuing calibration standards were ~~compared~~ evaluated against the new curve and found to meet method criteria. All of the samples for that day were then re-quanted against the new curve, as allowed by the method.

Signatures:

Analyst: Joseph E Talor   Date: 09-08-99

Laboratory Manager/Coordinator: Karen Riswold   Date: 9-8-99

Battelle QA/QC Officer: David B. Davis (acting)   Date: 9-7-99

Battelle Work Assignment Leader: Arthur Wszolek   Date: 9-7-99

P-5
QA Officer Site Visit Checklist

MSD Sewage Sludge Incinerator Plant
Site Visit Checklist

QA Officer _Susan J. Almay_

Work Assignment Manager Leader _Tony Wisbith_

Date _7-20-99_

QUALITY SYSTEM DOCUMENTATION

Is there an approved quality assurance project plan (QAPP) for the project and has it been reviewed by all appropriate personnel?	yes - approval sheet given to Tony Wisbith on-site w/ all approval signatures
Is a copy of the QAPP maintained at the field site?	yes
Is the design and conduct of the project as is specified in the QAPP?	yes
Are there deviations from the QAPP?	yes, these changes are to be documented on amendment sheet
How are any deviations from the QAPP noted?	See above
Briefly describe how calibration and other QC data are documented.	On ETS field sheets
Does the calibration documentation show that calibrations are being performed at the required frequency and in the required manner?	
Are the standard data forms dated?	yes

MSD Sewage Sludge Incinerator Plant Site Visit Checklist	
Is the person who recorded the data identified on the form?	yes)
Are any paper records written in indelible ink?	yes
Are the QC data reviewed by another qualified person such as the QA officer or the project leader? Who is this individual?	yes, Tony Wisbith
Is the project team adhering to the planned schedule? If not, explain the new schedule. Verify that all schedule changes have been authorized.	failed leak check on day #1 of sampling; resample begin ~3PM - dc per Gene R (on site
ORGANIZATION AND RESPONSIBILITIES	
Identify the following personnel and determine whether they have the listed responsibilities: Work Assignment Leader: responsible for overall performance of the project and communications with EPA Quality Assurance Officer: prepare QAPP; review and monitor QA activities Project Task Leader: responsible for the on-site emissions testing effort; supervision of all on-site and off-site staff and communication with other on-site personnel.	Gene Riley and Gene Crumpler on-site Tues. 7/20 (EPA) WAL - Tony Wisbith - on-site all week QAO - Susan abbsy on-site Mon Tues-Wed. Project Leader - Andy Hetz of ETS on-site all week
TRAINING AND SAFETY	
Is there special safety equipment required to ensure the health and safety of project personnel?	Samplers personnel should wear gloves when sampling inlet/outlet water. Told WAL

MSD Sewage Sludge Incinerator Plant Site Visit Checklist	
Is each project team member appropriately outfitted with safety gear?	All above. Otherwise steel-toed shoes, hard hats, safety glasses all ok
Are project personnel adequately trained for their safety during the performance of the project?	Yes
Who is authorized to halt emissions testing in the event of a health or safety hazard?	Yes
CORRECTIVE ACTION PROCEDURES	
Are there established procedures for corrective actions when the data quality indicator goals (e.g. out-of-control calibration data) are not met?	Yes, described in QAPP
Are the corrective action procedures consistent with the QAPP?	Yes, for example leak check failure
Have any such corrective actions been taken?	Yes, see above.

MSD Sewage Sludge Incinerator Plant Site Visit Checklist
Notes:

TECHNICAL REPORT DATA
(Please read Instructions on reverse before completing)

1 REPORT NO. EPA-454/R-00-038d	2.	3. RECIPIENT'S ACCESSION NO
4 TITLE AND SUBTITLE Source Characterization For Sewage Sludge Incinerators Final Emissions Report, Volume III of III, Appendix K - Appendix P Metropolitan Sewer District (MSD) Mill Creek Wasterwater Treatment Plant Cincinnati, Ohio		**5. REPORT DATE** September 2000
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Clyde E. Riley, USEPA Anthony S. Wisbith, Battelle Jeffery A. Ferg, Battelle Dennis A. Falgout, PES		**8. PERFORMING ORGANIZATION REPORT NO**
9. PERFORMING ORGANIZATION NAME AND ADDRESS Battelle 505 King Avenue Columbus, Ohio 43201-2693		**10. PROGRAM ELEMENT NO.**
		11. CONTRACT/GRANT NO. 68-D-99-009
12. SPONSORING AGENCY NAME AND ADDRESS Emissions, Monitoring and Analysis Division Office of Air Quality Planning and Standards U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711		**13. TYPE OF REPORT AND PERIOD COVERED** Final; January 99 to September 2000
		14. SPONSORING AGENCY CODE EPA/200/04

15. SUPPLEMENTARY NOTES

16 ABSTRACT

The Clean Air Act Amendments of 1990 require the U.S. Environmental Protection Agency's (EPA) Office of Air Quality Planning and Standards (OAQPS) to establish standards of performance for sewage sludge incineration. These standards are necessary to protect public health and the environment from any adverse effects of pollutant emissions from sewage sludge incineration. The regulations will contain general regulatory requirements, pollutant characterization, and emission limits. To assess control technologies as well as associated strategies for cost-effective standards, EPA requires data on PCB, D/F, and PAH emissions from sewage sludge incinerators . While some emission data exist for sewage sludge incinerators, data on coplanar polychlorinated biphenyls (PCBs) from sewage sludge incinerators are very limited.

The test report summarizes testing of a multiple hearth incinerator at the Metropolitan Sewer District (MSD) Mill Creek Wastewater Treatment Plant in Cincinnati, Ohio in July, 1999. The emission data collected in this test program will be used by EPA/OAQPS and EPA's Office of Water (OW) to support a decision about further data gathering efforts in support of MACT standards for sewage sludge incinerators. During the testing, a second EPA contractor monitored and recorded the process and emission control system operating parameters, and prepared Section 4.0, Process Description And Operation of the report. The report consist of five documents: Executive Summary Report; Volume I-Main Report; Volume II-Appendices A-J; Volume III-Appendices K-P; and a Data Quality Assessment Report.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	**b** IDENTIFIERS/OPEN ENDED TERMS	**c. COSATI** Field/Group
PCBs PAHs Dioxins/furans	Air Pollution control	
18. DISTRIBUTION STATEMENT Release Unlimited	**19. SECURITY CLASS** *(Report)* Unclassified	**21. NO. OF PAGES**
	20. SECURITY CLASS *(Page)* Unclassified	**22. PRICE**

EPA Form 2220-1 (Rev. 4-77)