

TABLE E-29. METALS ON HIGH VOLUME AIR FILTERS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: Ca (Continued)</u>				
22142	42.6	61.6	95.6	Z2133-42
22532	9.0	10.7	88.6	Z2528-32
23052	27.9	37.8	102.8	Z3051-59
23266	24.3	34.1	101.4	Z3265-69
23711	27.4	37.1	100.7	Z3709-13
24168	26.2	35.5	96.6	Z4160-68
24353	27.3	37.7	107.7	Z4351-66
24358	29.0	39.6	110.1	"
25465	14.0	19.1	103.9	Z5461-80
25479	19.8	25.3	112.5	"
25896	20.6	30.3	100.0	Z5895-98, Z5959-70
25966	22.4	32.0	99.2	"
26543	9.9	14.5	94.1	Z6542-51
		Mean	99.6 %	
		SD	7.7 %	
		cv	0 . 0 7 8	
<u>Parameter: Cd</u>				
Y1678	0.018	0.949	94.0	Y1674-80, Y1973-82
Y1681	0.014	0.120	107.2	Y1681-1711
Y1690	0.016	0.112	97.1	"
Y1698	0.018	0.112	95.1	"
Y1709	0.021	0.118	98.2	"
Y1864	co.020	0.194	98.0	Y1858-75
Y1874	0.023	0.216	97.6	"
Y1977	0.028	0.478	90.5	Y1674-80, Y1973-82
Y2102	co.050	0.449	90.2	Y2101-28
Y2116	co.050	0.449	90.2	"
Y2124	<0.050	0.469	94.3	"
Y2619	0.010	0.111	102-1	Y2618-35, Y2762-91
Y2627	0.023	0.129	107.3	"
Y2635	0.018	0.120	103.2	"

TABLE E-29. METALS ON HIGH VOLUME AIR FILTERS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recover,	Relevant Samples (Lab #s)
<u>Parameter: Cd (Continued)</u>				
Y2769	<0.010	0.118	119.2 *	Y2618-35, Y2762-91
Y2783	0.018	0.124	107.2	"
Y2787	0.028	0.134	107.3	"
Y3102	0.022	0.227	102.7	Y3101-34
Y3112	0.018	0.215	98.7	"
Y3124	0.031	0.128	98.3	"
Y3133	0.014	0.119	106.2	"
Y3370	0.018	0.123	106.2	Y3370-77, Y3735-52,
Y3736	0.027	0.125	99.2	Y4458-72
Y3747	0.011	0.113	103.1	"
Y4367	0.017	0.109	93.1	Y4360-84, Y4760-87
Y4377	0.026	0.120	95.2	"
Y4391	<0.010	0.103	104.0	Y4385-434, Y4462
Y4398	0.026	0.120	95.2	"
Y4403	0.011	0.114	104.1	"
Y4423	0.016	0.113	98.1	"
Y4430	0.018	0.113	96.1	"
Y4461	0.016	0.120	105.2	Y3370-77, Y3735-52,
Y4470	0.015	0.119	105.2	Y4458-72
Y4764	0.018	0.116	99.2	Y4360-84, Y4760-87
Y4775	0.026	0.126	101.4	"
Y4786	0.017	0.115	99.2	"
Y5151	<0.010	0.092	101.5	Y5148-91
Y5161	0.012	0.097	94.1	"
Y5172	0.011	0.096	94.0	"
Y5174	0.011	0.092	90.3	"
Y5179	0.010	0.096	105.0	"
Y5189	0.014	0.101	96.5	"
Y5616	0.016	0.034	93.4	Y5607-706
Y5623	0.012	0.028'	86.8	"
Y5639	co.010	0.096	96.6	"
Y5655	0.015	0.105	90.8	"
Y5666	0.017	0.106	90.0	"
Y5677	co.010	0.099	99.7	"
Y5692	<0.010	0.100	101.0	"
Y5696	co.010	0.093	93.9	"

\* Value greater than two standard deviations from mean

TABLE E-29. METALS ON HIGH VOLUME AIR FILTERS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: Cd (Continued)</u>				
Y5705	0.013	0.098	86.0	Y5607-706
Y6461	0.020	0.104	85.0	Y6461-87
Y6468	0.026	0.115	90.2	"
Y6478	0.012	0.106	95.1	"
Y6485	0.010	0.098	89.0	"
Y8245	<0.010	0.182	91.4	Y8241-64, Y8532-48,
Y8255	<0.010	0.187	93.9	Y8944-9114
Y8262	<0.010	0.187	93.9	"
Y8539	<0.010	0.199	99.9	"
Y8946	0.012	0.189	88.8	"
Y9113	<0.010	0.189	94.9	"
Y9823	<0.010	0.099	100.0	Y9819-36
Y9835	<0.010	0.101	102.0	"
20076	0.012	0.099	88.0	Z0074-89
Z0088	0.018	0.110	93.1	"
Z0765	<0.010	0.103	104.0	20764-94
Z0771	<0.010	0.095	96.0	"
Z0785	0.012	0.108	97.1	"
Z0792	0.010	0.118	109.2	"
Z1260	<0.010	0.103	104.0	Z1255-65, Z1523-25
Z1525	<0.010	0.106	107.6	"
Z1675	<0.010	0.211	105.7	Z1672-75
Z2141	0.012	0.101	90.0	Z2133-42
Z2737	0.015	0.113	99.1	Z2736-39
Z3051	<0.010	0.104	105.0	Z3051-59
Z3059	<0.010	0.105	106.1	Z3051-59
Z3711	<0.010	0.093	93.9	Z3709-13
Z4168	<0.010	0.096	97.0	Z4160-68
Z4351	0.011	0.098	88.6	Z4351-66
Z4357	<0.010	0.093	93.8	"
Z5465	<0.010	0.186	93.2	Z5461-80
Z5479	<0.010	0.212	106.9	"
Z5896	<0.010	0.197	98.7	Z5895-98, Z5959-70
Z5966	co.010	0.194	97.2	"
Z6542	co.010	0.455	91.5	Z6542-51
		Mean	97.9 %	
		SD	6.5 %	
		cv	0.066	

TABLE E-29. METALS ON HIGH VOLUME AIR FILTERS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recover	Relevant Samples (Lab #s)
<u>Parameter: Cr</u>				
Y1674	0.047	0.234	93.7	Y1674-80, Y1973-82
Y1681	0.059	0.268	105.8	"
Y1692	0.068	0.275	104.9	"
Y1701	0.386	0.563	91.3	"
Y1709	0.262	0.463	102.8	"
Y1861	0.066	0.257	96.8	Y1858-75
Y1865	0.105	0.302	100.0	"
Y1975	0.098	0.281	91.8	Y1674-80, Y1973-82
Y2101	0.102	0.288	93.3	Y2101-28
Y2107	0.087	0.270	91.8	"
Y2119	0.517	0.732	86.7	"
Y2631	0.083	0.301	109.3	Y2618-35, Y2762-91
Y2774	0.079	0.273	97.3	"
Y2781	0.054	0.238	92.2	"
Y2790	0.139	0.331	96.3	"
Y3102	0.154	0.344	95.3	Y3101-34
Y3103	1.851	3.614	88.5	"
Y3112	0.683	2.620	97.1	"
Y3113	0.055	0.244	94.7	"
Y3116	0.052	0.256	102.3	"
Y3120	0.556	2.725	108.7	"
Y3131	0.607	2.738	106.8	"
Y3132	0.059	0.241	91.2	"
Y3370	0.134	0.333	99.8	Y3370-77, Y3735-52,
Y3737	0.078	0.277	99.8	Y4458-72
Y3747	0.116	0.327	105.8	"
Y4366	0.057	0.254	98.8	Y4360-84, Y4760-87
Y4377	0.216	0.401	92.9	"
Y4392	0.051	0.255	102.2	Y4385-434, Y4462
Y4402	0.032	0.216	92.2	"
Y4412	0.051	0.241	95.2	"
Y4423	0.067	0.276	104.8	"
Y4462	0.067	0.269	101.3	"
Y4463	0.062	0.261	99.8	Y3370-77, Y3735-52,
Y4472	0-110	0.313	101.8	Y4458-72
Y4764	0.089	0.277	94.3	Y4360-84, Y4760-87

Final Rpt, Kuwait Oil Fire HRA No. 39-26-L192-91, 5 May - 3 Dec 91

TABLE E-29. METALS ON HIGH VOLUME AIR FILTERS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: Cr (Continued)</u>				
Y4775	0.236	0.277	20.8 • ☒	Y4360-84, Y4760-87
Y4786	0.209	0.409	100.4	"
Y5151	0.050	0.135	99.0	Y5148-91
Y5161	0.061	0.150	104.5	"
Y5172	0.090	0.164	90.7	"
Y5174	0.135	0.212	98.1	"
Y5179	0.040	0.121	92.3	"
Y5189	0.078	0.157	94.7	Y5148-91
Y5616	0.171	0.522	92.9	Y5607-706
Y5623	0.066	0.162	97.2	"
Y5629	0.178	0.260	84.0	"
Y5639	0.057	0.152	96.6	"
Y5655	0.090	0.189	100.3	"
Y5666	0.122	0.206	86.0	"
Y5677	0.080	0.175	97.4	"
Y5692	0.055	0.153	99.8	"
Y5696	0.034	0.136	103.2	"
Y5705	0.118	0.219	103.2	"
Y6461	0.166	0.260	96.6	Y6461-87
Y6468	0.277	0.356	82.6 •	"
Y6478	0.108	0.206	100.1	"
Y6485	0.097	0.183	87.8	"
Y8245	0.046	0.229	92.0	Y8241-64, Y8532-48,
Y8255	0.064	0.247	92.0	Y8944-9114
Y8262	0.059	0.240	91.0	"
Y8539	0.040	0.237	99.0	"
Y8946	0.077	0.264	94.0	"
Y9113	0.039	0.223	92.4	"
Y9823	0.044	0.140	97.4	Y9819-36
Y9835	0.030	0.127	98.3	"
zoo74	0.061	0.154	94.5	Z0074-89
20075	0.113	0.201	90.0	"
Z0087	0.136	0.221	87.2	"
20765	0.034	0.131	98.3	Z0764-94
20771	0.035	0.134	100.3	"

\* Value greater than two standard deviations from mean  
• \* Outlier, excluded from statistics

TABLE E-29. METALS ON HIGH VOLUME AIR FILTERS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: Cr (Continued)</u>				
20785	0.136	0.229	95.3	Z0764-94
20792	0.080	0.172	93.7	"
21260	0.069	0.164	97.2	Z1255-65, Z1523-25
21525	0.048	0.144	97.4	"
21675	0.056	0.249	96.8	Z1672-75
22141	0.045	0.143	99.4	Z2133-42
22737	0.104	0.214	112.1 *	Z2736-39
23051	0.067	0-165	99.7	Z3051-59
23059	0.063	0.166	104.7	Z3051-59
23711	0.029	0.123	95.2	Z3709-13
24168	0.033	0.130	98.3	Z4160-68
24354	0.025	0.035	105.5	Z4351-66
24364	0.035	0.053	93.8	"
25467	0.045	0.252	103.8	Z5461-80
25477	0.033	0.245	106.3	"
25899	<0.020	0.214	107.2	Z5895-98, Z5959-70
25967	0.021	0.232	105.7	"
26542	co.020	0.465	93.5	Z6542-51
		Mean	97.4 %	
		SD	6.0 %	
		cv	0.061	
<u>Parameter: Fe</u>				
Y9823	6.06	7.94	94.8	Y9819-36
Y9835	5.16	7.21	103.2	"
zoo74	14.50	24.70	103.2	Z0074-89
zoo75	26.70	35.40	88.8	"
20765	8.84	13.60	96.6	Z0764-94
Z0775	9.57	14.10	92.0	"
20785	21.50	26.00	92.6	"
20793	9.88	14.90	101.9	"
Z1258	4.88	9.51	93.6	Z1255-65, Z1523-25

\* Value greater than two standard deviations from mean

Final Rpt, Kuwait Oil Fire HRA No. 39-26-L192-91, 5 May - 3 Dec 91

TABLE E-29. METALS ON HIGH VOLUME AIR FILTERS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: Fe (Continued)</u>				
21525	10.80	15.60	97.6	Z1255-65, Z1523-25
21674	19.56	28.29	90.1	Z1672-75
22134	7.52	10.08	105.4	Z2133-42
22532	0.30	0.76	92.8	Z2528-32
23052	5.41	7.32	96.2	Z3051-59
23267	6.64	8.65	101.4	Z3265-69
Z3711	6.03	7.92	95.3	Z3709-13
24167	12.50	14.60	106.5	Z4160-68
24354	4.94	6.87	103.4	Z4351-66
24357	6.06	9.91	106.0	"
25464	2.26	4 . 2 4	99.4	Z5461-80
25471	3.64	5.66	101.6	"
25895	4.84	6.74	95.7	Z5895-98, Z5959-70
25964	2.15	4.03	94.4	"
26542	1.22	1.72	101.7	Z6542-51
		Mean	98.1 %	
		SD	5.2 %	
		cv	0.053	

<u>Parameter: Mg</u>				
Y9 824	1.62	2.59	99.6	Y9819-36
Y9835	6.92	11.80	98.8	"
Z0076	10.30	15.80	111.6	Z0074-89
20765	13.00	17.80	97.8	Z0764-94
20770	9.87	15.20	108.1	"
20784	16.50	21.70	106.2	"
20787	8.34	13.60	106.6	"
21258	8.62	13.70	103.0	Z1255-65, Z1523-25
21525	11.90	17.20	107.7	"
21675	24.80	35.00	105.5	Z1672-75
22142	7.15	11.70	92.2	Z2133-42
22532	2.45	4.30	92.9	Z2528-32
23052	7.84	9.86	102.0	Z3051-59
23266	7.75	9.74	100.5	Z3265-69
23711	6.54	8.48	97.9	Z3709-13

TABLE E-29. METALS ON HIGH VOLUME AIR FILTERS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: Mg (Continued)</u>				
24168	6.77	8.67	95.9	Z4160-68
24354	6.59	8.76	109.4	Z4351-66
24362	2.87	4.69	91.5	"
25465	3.38	5.38	100-s	Z5461-80
Z5479	4.68	6.50	91.7	"
Z5896	3.35	5.54	110.1	Z5895-98, Z5959-70
25966	5.93	8.08	108.3	"
26543	3.85	4.7s	94-8	Z6542-51
		Mean	101.4 %	
		SD	6.4 %	
		CV	0.063	
<u>Parameter: Na</u>				
Y9824	60.6	80.8	101.8	Y9819-36
Y9829	41.3	60.4	96.1	"
Z0078	64.3	85.2	106.2	Z0074-89
20764	81.0	100.0	96.0	Z0764-94
Z0775	62.2	79.2	85.8	"
20777	36.7	56.4	99.1	"
20786	32.1	51.5	97.5	"
Z0078	64.3	85.2	106.2	Z0074-89
21258	sf.8	77.6	109.8	Z1255-65, Z1523-25
21523	12.0	17.4	109.7	"
21674	23.0	33.9	111.5	Z1672-75
22137	47.2	65.1	90.2	Z2133-42
Z2736	48.3	69.9	108.7	Z2736-39
23052	18.9	28.7	100.9	Z3051-59
23265	22.3	31.4	94.1	Z3265-69
23710	20.6	30.3	100.0	Z3709-13
24167	18.0	27.7	99.8	Z4160-68
24354	5.7	7.7	102.8	Z4351-66
24360	4.7	6.5	92.2	"
25466	4.0	6.2	108.6	Z5461-80
25479	5.6	7.6	101.3	"
Z5898	5.6	7.4	95.7	Z5895-98, Z5959-70

TABLE E-29. METALS ON HIGH VOLUME AIR FILTERS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: Na (Continued)</u>				
25970	7.0	8.9	94.4	Z5895-98, Z5959-70
Z6545	10.9	16.4	111.6	Z6542-51
		Mean	100.6 %	
		SD	7.2 %	
		cv	0-071	
<u>Parameter: Ni</u>				
Y1674	0.147	0.295	77.0	Y1674-80, Y1973-82
Y1681	0.054	0.525	94.7	Y1681-1711
Y1692	0.050	0.499	100.3	"
Y1702	0.051	0.526	95.5	"
Y1707	0.107	0.567	92.6	"
Y1861	0.090	0.582	99.0	Y1858-75
Y1872	0.079	0.542	93.1	"
Y1974	0.209	0.389	93.9	Y1674-80, Y1973-82
Y2101	0.104	0.276	88.8	Y2101-28
Y2111	0.499	0.660	87.1	"
Y2124	0.551	0.715	89.2	"
Y2618	0.104	0.548	89.4	Y2618-35, Y2762-91
Y2633	0.082	0.548	93.8	"
Y2633	0.082	0.537	91.5	"
Y2773	0.091	0.569	96.2	"
Y2780	0.064	0.556	99.0	"
Y2788	0.085	0.550	93.6	"
Y3102	0.179	0.637	92.2	Y3101-34
Y3109	0.142	0.630	98.2	Y3101-34
Y3123	0-198	0.660	93.1	"
Y3134	0-064	0.526	92.9	"
Y3370	0.157	0.588	86.8	Y3370-77, Y3735-52,
Y3737	0.087	0.543	91.7	Y4458-72
Y3747	0.089	0.552	93.2	"
Y4368	co.050	0.487	97.9	Y4360-84, Y4760-87
Y4391	0.172	0.253	83.5	Y4385-434, Y4462
Y4395	0.316	0.493	93.4	"
Y4408	0.132	0.222	92.2	"

TABLE E-29. METALS ON HIGH VOLUME AIR FILTERS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab amp le#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: Ni (Continued)</u>				
Y4415	0.077	0.170	94.7	Y4385-434, Y4462
Y4424	0.239	0.408.	88.6	"
Y4425	0.138	0.319	93.1	"
Y4432	0.100	0.192	93.9	"
Y4463	0.081	0.546	93.6	Y3370-77, Y3735-52,
Y4472	0.100	0.556	91.8	Y4458-72
Y4764	0.131	0.600	94.4	Y4360-84, Y4760-87
Y4774	0.201	0.648	90.0	"
Y4787	0.143	0.606	93.2	"
Y5151	0.050	0.131	93.7	"
Y5161	0.144	0.219	96.8	"
Y5174	0.114	0.184	88.8	"
Y5179	0.058	0.161	118.8 •	"
YS189	0.104	0.191	106.1	"
Y5616	0.272	0.616	92.4	Y5607-706
YS623	0.120	0.202	83.4	"
Y5629	0.242	0.339	100.3	"
Y5655	0.103	0.193	91.9	"
Y5666	0.166	0.267	103.5	"
YS677	0.086	0.178	93.8	"
Y5696	0.057	0.154	98.4	"
Y5705	0.215	0.294	82.1	"
Y6461	0.278	0.350	75.5 •	Y6461-87
Y6468	0.447	0.522	80.2	"
Y6478	0.127	0.223	98.2	"
Y6485	0.120	0.199	81.0	"
Y8241	0.328	0.509	91.5	Y8241-64, Y8532-48,
Y8245	0.049	0.260	106.0	Y8944-9114
Y8256	0.288	0.498	106.0	"
Y8548	0.237	0.435	99.9	"
Y8946	0.371	0.561	96.1	"
Y9114	0.353	0.544	96.6	"
Y9835	<0.050	0.095	96.0	Y9819-36
zoo74	0.061	0.159	98.8	Z0074-89
Z0075	0.146	0.231	86.2	"
20765	<0.050	0.110	111.1	Z0764-94

\* Value greater than two standard deviations from mean

TABLE E-29. METALS ON HIGH VOLUME AIR FILTERS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: Ni (Continued)</u>				
Z0771	0.050	0.083	83.8	Z0764-94
20785	0.193	0.284	93.8	"
20792	0.108	0.198	92.0	"
21260	0.586	0.632	52.4 *	Z1255-65, Y1523-25
21525	0.416	0.493	82.1	"
Z1675	0.541	0.736	98.2	Z1672-75
22141	0.594	0.681	93.8	Z2133-42
22737	0.436	0.537	106.4	Z2736-39
23051	0.402	0.591	95.1	Z3051-59
23059	0.357	0.457	104.6	Z3051-59
Z3711	0.343	0.433	94.3	Z3709-13
24168	0.384	0.836	91.2	Z4160-68
Z4355	<0.050	0.377	98.1	Z4351-66
24361	0.081	0.131	97.5	"
25467	0.279	0.467	94.5	Z5461-80
Z5477	0.368	0.546	89.6	"
Z5959	0.227	0.423	98.4	Z5895-98, Z5959-70
25967	0.150	0.331	90.8	"
Z6542	0.062	0.597	107.6	Z6542-51
		Mean	93.5 %	
		SD	7.2 %	
		CV	0.077	
<u>Parameter: Pb</u>				
Y1678	0.848	1.876	104.7	Y1674-80, Y1973-82
Y1681	1.551	2.001	92.0	Y1681-1711
Y1685	2.318	3.256	97.1	"
Y1698	1.630	2.556	95.2	"
Y1709	2.738	3.666	96.5	"
Y1860	0.988	3.073	105.8	Y1858-75
Y1875	1.171	2.943	90.1	"
Y1977	0.709	1.244	108.2	: Y1674-80, Y1973-82

\* Value greater than two standard deviations from mean

TABLE E-29. METALS ON HIGH VOLUME AIR FILTERS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: Pb (Continued)</u>				
Y2102	0.926	1.459	108.1	Y2101-28
Y2116	1.595	2.108	104.7	"
Y2124	1.797	2.307	104.3	"
Y2618	1.997	3.830	92.0	"
Y2632	0.512	2.439	96.6	Y2618-35, Y2762-91
Y2770	0-241	2.119	94.1	"
Y2781	0.479	2.425	97.5	"
Y2787	0.329	2.292	98.4	"
Y3370	7.320	9.284	99.1	Y3370-77, Y3735-52,
Y3737	0.925	2.860	97.0	Y4458-72
Y3743	0.616	2.553	97.1	"
Y4368	0-365	2.363	100.1	Y4360-84, Y4760-87
Y4375	0.285	2.120	92.0	"
Y4379	2.046	3.967	96.4	"
Y4386	0.988	2.950	98.4	Y4385-434, Y4462
Y4402	0.258	2.480	111.4	"
Y4412	1.030	3.170	107.3	"
Y4422	0.375	2.460	104.5	"
Y4430	0.741	2.790	102.7	"
Y4463	0,454	2.426	98.8	Y3370-77, Y3735-52,
Y4472	0.547	2.723	109.1	Y4458-72
Y4773	0.610	2.569	98.2	Y4360-84, Y4760-87
Y4787	0.722	2.519	90.1	"
Y5157	0.715	1.113	110.6	Y5148-91
Y5158	1.072	1.957	90.5	"
Y5171	1.013	1.828	83.3	Y5148-91
Y5181	1.433	2.999	81.3 *	"
YS608	3.740	5.308	83.7	Y5607-706
Y5617	1,122	1.932	82.9 *	"
YS623	0.463	0.658	104.1	"
Y5638	0.286	0.382	99.8	"
YS648	0.383	0.483	104.8	"
Y5653	2.253	3.135	91.3	"
Y5670	0.922	1.214	85.1	"
Y5690	0.598	0.783	100.3	"
Y5700	1.938	2.781	87.1	"

\* Value greater than two standard deviations from mean

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TABLE E-29. METALS ON HIGH VOLUME AIR FILTERS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: Pb (Continued)</u>				
Y6462	0.600	0.956	98.6	Y6461-87
Y6468	1.040	1.890	86.9	"
Y6480	1.100	2.080	100.1	"
Y6486	4.390	6.100	91.6	"
Y8241	1.650	6.500	97.6	Y8241-64, Y8532-48,
Y8251	1.170	3.250	104.3	Y8944-9114
Y8261	3.140	5.220	104.5	"
Y8538	0.399	2.610	110.8	"
Y8945	0.968	3.170	110.4	"
Y9106	1.040	3.120	104.3	"
Y9823	0.789	2.680	94.8	Y9819-36
Y9835	-0.846	2.790	97.5	"
Z0076	1.310	3.430	106.3	Z0074-89
Z0088	2.890	4.890	100.5	"
Z0765	0.291	2.200	95.7	Z0764-94
Z0775	1.950	3.820	93.9	"
Z0785	1.080	2.950	93.8	"
Z0793	2.640	4.640	100.5	"
Z1258	0.274	1.150	88.8	Z1255-65, Y1523-25
Z1525	0.421	1.300	89.2	"
Z1672	1.232	1.675	92.0	Z1672-75
Z2135	0.944	1.429	99.9	Z2133-42
Z2137	2.290	3.207	98.1	Z2133-42
Z2736	1.560	3.440	97.4	Z2736-39
Z3052	0.816	2.880	103.5	Z3051-59
Z3267	2.550	4.570	101.5	Z3265-69
Z3711	3.410	5.290	94.5	Z3709-13
Z4167	2.890	4.660	89.0	Z4160-68
Z4354	0.782	2.790	100.7	Z4351-66
Z4362	0.531	2.590	103.2	"
Z5464	2.320	4.290	98.9	Z5461-80
Z5471	2.810	4.950	107.5	"
Z5895	2.010	3.800	89.9	Z5895-98, Z5959-70
Z5964	2.130	3.930	90.4	"
Z6542	0.380	0.851	95.1	Z6542-51
		Mean	97.8 %	
		SD	7.2 %	
		CV	0.073	

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TABLE E-29. METALS ON HIGH VOLUME AIR FILTERS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: V</u>				
Y1676	0.050	0.525	105.5	Y1674-80, Y1973-82
Y1681	0.053	0.456	85.1 *	Y1681-1711
Y1686	0.128	0.557	91.4	"
Y169.6	0.070	0.516	94.3.	"
Y1705	0.236	0.682	96.1	"
Y1831	<0.050	0.458	96.3	Y1858-75
Y1860	0.096	0.566	99.7	"
Y1865	0.116	0.633	109.9	"
Y1874	0.106	0.584	101.4	"
Y1981	0.066	0.544	96.1	Y1674-80, Y1973-82
Y2104	0.091	0.598	102.0	Y2101-28
Y2111	0.218	0.714	99.9	Y2101-28
Y2125	0.072	0.583	102.8	"
Y2618	0.047	0.526	96.3	Y2618-35, Y2762-91
Y2618	0.116	0.298	91.3	"
Y2622	0.089	0.292	101.8	"
Y2630	0.055	0.569	103.4	"
Y2767	0.078	0.594	103.8	"
Y2778	0.069	0.569	100.6	"
Y2782	0.096	0.567	94.8	"
Y3103	0.180	0.674	99.5	Y3101-34
Y3112	0.141	0.666	105.7	"
Y3123	0.087	0.595	102.2	"
Y3133	0.136	0.666	106.7	"
Y3370	0.084	0.619	107.6	Y3370-77, Y3735-52,
Y3735	0.067	0.583	103.8	Y4458-72
Y3746	0.059	0.537	96.1	"
Y4367	0.079	0.555	95.8	Y4360-84, Y4760-87
Y4378	0.077	0.596	104.4	"
Y4392	0.066	0.547	96.8	Y4385-434, Y4462
Y4402	0.061	0.524	93.1	"
Y4411	0.061	0.542	96.7	"
Y4423	0.057	0.532	95.5	"
Y4433	0.053	0.532	96.3	"
Y4461	0.083	0.563	96.6	Y3370-77, Y3735-52,
Y4471	0.080	0.547	94.0	Y4458-72

\* Value greater than two standard deviations from mean

TABLE E-29. METALS ON HIGH VOLUME AIR FILTERS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: V (Continued)</u>				
Y4765	0.055	0.582	106.0	Y4360-84, Y4760-87
Y4776	0.068	0.592	105.4	"
Y4787	0.094	0.593	100.4	"
Y5157	0.053	0.501	90.1	Y5148-91
Y5167	0.075	0.572	100.0	"
Y5178	0.146	0.636	98.6	"
Y5190	0.219	0.720	100.9	"
Y5610	0.110	0.198	90.2	Y5607-706
Y5619	0.183	0.272	92.5	"
Y5628	0.232	0.319	90.3	"
Y5639	co.050	0.110	111.6 *	"
Y5652	0.056	0.148	93.8	"
Y5658	0.075	0.164	90.2	"
Y5676	0.091	0.181	91.2	"
Y5685	0.146	0.231	87.2	"
Y5696	0,083	0.172	90.1	"
Y6463	0.127	0.618	98.8	Y6461-87
Y6474	0.061	0.600	108.4	"
Y6487	0.063	0.586	105.2	"
Y8245	0.084	0.272	94.5	Y8241-64, Y8532-48,
Y8255	co.050	0.239	120.0 *	Y8944-9114
Y8262	0.029	0.223	97.4	"
Y8539	0.052	0.251	100.0	"
Y8946	0.092	0.277	93.0	"
Y9113	<0.050	0.211	105.9	"
Y9821	0.071	0.161	91.6	Y9819-36
Y9832	0.089	0.180	92.8	"
20075	0.090	0.556	93.8	Z0074-89
20089	0.136	0.621	97.6	"
20764	0.092	0.184	93.8	Z0764-94
20774	0.062	0.161	100.6	"
20784	0.056	0.146	91.5	"
20794	0.069	0.166	98.7	"
Z1260	0.088	0.183	96.5	Z1255-65, Y1523-25
Z1525	0.056	0.159	104.2	"
Z1675	0.058	0.251	96.8	Z1672-75

\* Value greater than ± standard deviations from mean

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TABLE E-29. METALS ON HIGH VOLUME AIR FILTERS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: V (Continued)</u>				
22141	0.076	0.167	92.7	Z2133-42
22737	0.094	0.190	97.9	Z2736-39
Z3051	0.051	0.152	102.5	Z3051-59
23059	0.084	0.176	93.8	Z3051-59
23711	0.054	0.144	91.4	Z3709-13
24352	co.050	0.208	106.3	Z4351-66
24362	co.050	0.199	101.3	"
25467	co.050	0.212	106.2	Z5461-80
25477	co.050	0.240	104.2	"
Z5959	<0.050	0.223	103.2	Z5895-98, Z5959-70
25967	<0.050	0.212	106.2	"
26550	co.050	0.494	99.3	Z6542-51
		Mean	98.7 %	
		SD	6.2 %	
		CV	0.062	
<u>Parameter: Zn</u>				
Y1674	o-337	0.507	90.1	Y1674-80, Y1973-82
Y1682	1.770	3.754	101.1	Y1681-1711
Y1684	0.534	1.414	102.1	"
Y1695	0.623	1.076	101.4	"
Y1706	0.390	0.848	100.1	"
Y1859	1.523	3.360	93.5,	Y1858-75
Y1860	0.586	1.000	92.8	"
Y1865	0.320	0.762	96.0	"
Y1974	0.311	0.522	110.7	Y1674-80, Y1973-82
Y2102	0.264	0.441	92.9	Y2101-28
Y2112	0.383	0.543	85.4 •	"
Y2115	1.004	1.333	92.5	"
Y2122	0,746	1.063	89.9	"
Y2619	0.383	0.483	104.8	Y2618-35, Y2762-91
Y2627	0.562	0.654	98.5	"

• Value greater than two standard deviations from mean

TABLE E-29. METALS ON HIGH VOLUME AIR FILTERS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: Zn (Continued)</u>				
Y2635	0.285	0.377	95.8	Y2618-35, Y2762-91
Y2769	0.166	0.271	107.7	"
Y2783	0.383	0.487	108.9	"
Y2787	0.316	0.417	105.2	"
Y3102	0.411	0.607	98.6	Y3101-34
Y3112	0.276	0.459	92.0	"
Y3124	0.362	0.458	100.6	"
Y3133	0.237	0.332	98.3	"
Y3370	0.370	0.464	98.6	Y3370-77, Y3735-52,
Y3736	0.342	0.431	93.3	Y4458-72
Y3747	0.210	0.305	98.0	"
Y4368	0.197	0.284	89.8	Y4360-84, Y4760-87
Y4378	0.464	0.561	102.6	"
Y4385	0.258	0.355	100.6	Y4385-434, Y4462
Y 4 3 8 5	0.139	0.227	90.3	"
Y4397	0.258	0.355	100.6	"
Y4410	0.185	0.274	91.7	"
Y4416	0.353	0.446	97.5	"
Y4425	0.184	0.272	90.7	"
Y4434	0.175	0.271	98.7	"
Y4461	0.226	0.325	102.2	Y3370-77, Y3735-52,
Y4470	0.212	0.314	105.1	Y4458-72
Y4764	0.671	0.767	103.7	Y4360-84, Y4760-87
Y4774	0.216	0.322	109.2	"
Y4787	0.367	0.467	104.7	"
Y5151	0.139	0.208	89.5	Y5148-91
Y5161	0.377	0.434	99.6	"
Y5172	0.271	0.333	96.1	"
Y5174	0.181	0.242	85.1 *	"
Y5179	0.162	0.236	97.0	"
Y5189	0.344	0.411	107.9	"
Y5616	0.331	0.704	100.3	Y5607-706
Y5623	0.330	0.432	105.8	"
Y5629	0.489	0.577	94.1	"
Y5639	0.190	0.289	102.3	"
Y5655	0.582	0.676	101.5	"

\* Value greater than two standard deviations from mean

TABLE E-29. METALS ON HIGH VOLUME AIR FILTERS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: Zn (Continued)</u>				
Y5666	0.338	0.421	87.0	Y5607-706
Y5677	0.569	0.662	100.1	"
Y5692	0.304	0.406	106.2	"
Y5696	0.376	0.478	107.2	"
Y6461	0.309	0.401	96.0	Y6461-87
Y6468	0.397	0.493	100.9	"
Y6478	0.313	0.421	112.2	"
Y6485	0.432	0.525	98.2	"
Y8245	0.046	0.229	92.0	Y8241-64, Y8532-48,
Y8255	0.065	0.253	94.5	Y8944-9114
Y8262	0.054	0.242	94.5	"
Y8539	0.036	0.238	101.5	"
Y8946	0.081	0.260	90.0	"
Y9113	0.034	0.217	91.9	"
Y9823	0.221	0.319	101.2	Y9819-36
Y9835	0.227	0.335	111.4	"
zoo74	0.056	0.150	95.5	Z0074-89
Z0087	0.137	0.226	91.3	"
20765	0.362	0.456	98.6	Z0764-94
20771	0.366	0.468	106.7	"
Z0785	0.501	0.596	101.0	"
20792	0.347	0.445	102.4	"
21260	0.300	0.391	94.3	Z1255-65, Y1523-25
21525	0.231	0.320	92.1	"
21675	0.058	0.251	96.8	Z1672-75
22141	0.076	0.167	92.7	Z2133-42
22737	0.094	0.190	97.9	Z2736-39
23051	0.051	0.152	102.5	Z3051-59
23059	0.084	0.176	93.8	Z3051-59
23711	0.054	0.144	91.4	Z3709-13
24352	co.050	0.208	106.3	Z4351-66
24362	co.050	0.199	101.3	"
Z5467	co.050	0.212	106.2	Z5461-80
25477	<0.050	0.240	104.2	"

• Value greater than two standard deviations from mean

TABLE E-29. METALS ON HIGH VOLUME AIR FILTERS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: Zn (Continued)</u>				
25959	<0.050	0.223	103.2	Z5895-98, Z5959-70
25967	<0.050	0.212	106.2	"
26550	<0.050	0.494	99.3	Z6542-51
		Mean	98.7 %	
		SD	6.2 %	
		cv	0.062	

TABLE E-30. METALS ON CELLULOSE ESTER FILTERS

Instrument Duplicate Analysis Data  
(units are mg/L)

Param.	Lab Sample #	Value 1	Value 2	% RPD	Relevant Samples (Lab #s)
Ca	Y3068	0.131	0.150	13.5	Y3067-8
V	Y3366	co.050	co.050	0.0	Y1830-32, Y2611-17 and Y3366-67

Post-Digested Instrument Spike Data  
(units are mg/L)

Param.	Lab Sample #	Value 1	Value 2	% Recovery	Relevant Samples (Lab #s)
Ca	Y3068	0.131	0.669	108.27	Y3067-8
V	Y3366	co.050	0.499	100.30	Y1830-32, Y2611-17 and Y3366-67

TABLE E-31. MERCURY TUBES FORMERCURY

Internal Controls (Desorption Efficiencies)  
(units are mg)

Method	Prepped Sample	Unspiked Amount	Spiked Amount	mg Added	% Recovery	Relevant Samples
Cold Vapor	Blank	0.000	0.090	0.25	36.0	Y7422-34,
	"	0.000	0.035	0.10	35.0	Y8135-49
	"	0.000	0.045	0.05	90.0	"
	"	0.000	0.030	0.15	20.0	"
	"	0.000	0.085	0.40	21.3	"
	"	0.000	0.050	0.08	62.5	"
	"	0.000	0.030	0.10	30.0	"
	"	0.000	0.035	0.05	70.0	"
			Average		45.6%	
	Blank	0.000	1.50	1.00	150.0	Y8521-31,
	"	0.000	2.13	1.50	142.0	Y8937-43,
			Average		146%	Y9094-99
	Blank	0.000	0.002	0.005	40.0	Y9769-92, Z0020-38

External Quality Controls  
(units are mg)

Method	Prepped Sample	Unspiked Amount	Spiked Amount	mg Added	% Recovery	Relevant Samples
Hydride	Blank	0.00000	0.00132	0.0020	66.00	Z0889-0924
	"	0.00000	0.00062	0.0010	62.00	"
	"	0.00000	0.00120	0.0010	120.00	Z1241-53
	"	0.00000	0.00220	0.0020	110.00	"
	"	0.00000	0.00172	0.0015	114.67	"
	"	0~00000	0.00090	0.0010	90.00	Z1511-18
			Mean		93.7%	
			SD		25.2%	
			CV		0-269	

TABLE E-32. MERCURY TUBES FORMERCURY

Instrument Duplicate Analysis Data  
(units are mg/L)

Method	Lab Sample #	Value 1	Value 2	% RPD	Relevant Samples (Lab #s)
Cold Vapor	Y7422	0.0004	0.0004	0.00	Y7422-34
	Y7429	0.0004	0.0004	0.00	"
	Y8137	0.0004	0.0004	0.00	Y8135-49
	Y8141	0.0004	0.0004	0.00	"
	Y8526	0.0009	0.0008	11.76	Y8521-31
	Y8531	0.0004	0.0005	22.22	"
	Y8941	0.0006	0.0005	18.18	Y8937-43
	Y9774	0.0018	0.0017	5.71	Y9769-92
	Y9784	0.0018	0.0017	5.71	"
	Z0020	0.0009	0.0009	0.00	Z0020-38
	zoo31	0.0007	0.0006	15.38	"
	20889	0.0009	0.0009	0.00	Z0889-0924
	20897	0.0011	0.0011	0.00	"
	20903	0.0002	0.0003	40.00	"
Hydride	20908	<0.0002	<0.0002	0.00	Z0889-0924
	20923	<0.0002	<0.0002	0.00	"
	Z1243	<0.0002	<0.0002	0.00	Z1241-53
	Z1246	<0.0002	<0.0002	0.00	"
	Z1511	<0.0002	<0.0002	0.00	Z1511-18
	Z1516	<0.0002	<0.0002	0.00	"

TABLE E-33. MERCURY TUBES FOR MERCURY

Post-Digested Instrument Spike Data  
(units are mg/L)

Method	Lab Sample #	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)	
Cold Vapor	Y7423	0.0004	0.0007	27.5	Y7422-34	
	Y7429	0.0004	0.0007	30.5	"	
	Y8138	0.0008	0.0011	17.5	Y8135-49	
	Y8142	0.0004	0.0007	27.5	"	
	Y8526	0.0009	0.0014	47.0	Y8521-31	
	Y8529	0.0007	0.0012	46.0	"	
	Y8530	0.0010	0.0019	81.5	"	
	Y8941	0.0006	0.0012	50.6	Y8937-43	
	Y9775	0.0016	0.0021	90.5	Y9769-92	
	Y9787	0.0016	0.0021	90.5	"	
	zoo31	0.0005	0.0010	85.0	Z0020-38	
	20893	0.0008	0.0017	80.5	Z0889-0924	
	Hydride	20905	<0.0002	0.0093	93.0	Z0889-0924
		20910	<0.0002	0.0096	96.0	"
21242		<0.0002	0.0106	106.0	Z1241-53	
21250		0-0002	0-0090	89.0	"	
21512		<0.0002	0.0087	87.0	Z1511-1518	
Z1518		<0.0002	0.0080	80.0	"	
			Mean	68.1 %		
			SD	28.6 %		
			CV	0.420		

TABLE E-34. RESPIRABLE SILICA ON PVC FILTERS

Controls Analyzed (NIOSH PAT Samples)	% Recovery	Relevant Samples (Lab #s)
!1200(101-2)	88.6	N2756-68

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TABLE E-35. METALS IN SOILS

External Controls						
Spike Param.	Prepped Sample #	Unspiked Amount	Spiked Amount	mg Added	% Recovery	Relevant Samples
Al	EPA-LCS	NA	325	298	92	Y2165-90
	Y2167	9140	9590	200	225	"
	Y2179	2490	2070	200	0	"
	Y4850	4000	5300	200	650	Y4846-54
	Y6710	4250	5660	300	470	Y6705-14
	26822	1700	1920	160	138	Z6819-31
	26828	2600	2920	160	200	"
As	EPA-LCS	NA	917	975	94.1	Y2165-90
	Y2167	3.7	187	200	91.7	"
	Y2179	1.7	185	200	91.6	"
	Y4850	3.2	224	200	110.4	Y4846-54
	Y6710	2.0	307	300	101.7	Y6705-14
	zoo93	co.7	402	400	100.5	Z0090-94
	20693	1.2	398	400	99.2	Z0684-723
	20704	1.6	400	400	99.6	"
	20717	1.5	402	400	100.1	"
	Z0722	2.4	375	400	93.2	"
	21666	0.9	390	400	97.3	Z1664-71
	26822	1.2	4.1	4.0	72.5	Z6819-31
	26828	2.4	6.6	4.0	105.0	"
				Mean	96.7%	
				SD	9.0%	
			cv	0.093		

TABLE E-35. METALS IN SOILS (Continued)

External Controls						
Spike Param.	Prepped Sample #	Unspiked Amount	Spiked Amount	mg Added	% Recovery	Relevant Samples
Be	EPA-LCS	NA	19.4	18.9	102.6	Y2165-90
	Y2167	1.6	5.8	5.0	84.6	"
	Y2179	0.4	4.0	5.0	72.9	"
	Y4850	0.8	5.1	5.0	86.4	Y4846-54
	Y6710	0.7	7.0	7.5	84.4	Y6705-14
	20093	1.2	9.2	10.0	80.0	Z0090-94
	20693	0.3	9.0	10.0	87.5	Z0684-723
	20704	0.4	8.4	10.0	80.0	"
	20717	0.2	9.1	10.0	89.2	"
	20722	0.5	8.1	10.0	75.5	"
	21666	co.2	8.2	10.0	82.0	Z1664-71
	26822	co.4	2.2	2.0	110.0	Z6819-31
	26828	co.4	2.2	2.0	110.0	"
				Mean	88.1%	
				SD	12.1%	
			CV	0.137		
Ca	EPA-LCS	NA	196	200	98	Y2165-90
	26822	59000	66000	2000	350	Z6819-31
	26828	30000	26000	2000	0	"

TABLE E-35. METALS IN SOILS (Continued)

External Controls

Spike Param.	Prepped Sample #	Unspiked Amount	Spiked Amount	mg Added	% Recovery	Relevant Samples
Cd	EPA-LCS	NA	45.4	45.0	100.9	Y2165-90
	Y2167	5.7	9.7	5.0	79.6	"
	Y2179	1.9	9.7	5.0	155.0	"
	Y4850	<2.0	6.9	5.0	137.2	Y4846-54
	Y6710	<1.8	8.6	7.5	114.5	Y6705-14
	zoo93	9.7	9.6	10.0	0.0 *	20090-94
	20693	<1.9	10.0	10.0	100.0	Z0684-723
	20704	2.6	11.0	10.0	84.0	"
	Z0717	<2.0	10.0	10.0	100.0	"
	20722	4.1	11.0	10.0	69.0	"
	21666	3.5	13.0	20.0	47.5	Z1664-71
	26822	<1.9	2.8	2.0	140.0	Z6819-31
	26828	<2.0	3.2	2.0	160.0	"
				Mean	107.3%	
			SD	35.1%		
			CV	0.327		
Cr	EPA-LCS	NA	99.6	106.0	94.0	Y2165-90
	Y2167	31.9	50.6	20.0	93.5	"
	Y2179	10.4	26.9	20.0	82.5	"
	Y4850	22.5	44.1	20.0	108.0	Y4846-54
	Y6710	53.4	43.9	30.0	77.3	Y6705-14
	zoo93	12.0	42.9	40.0	65.0	Z0090-94
	20693	47.0	73.0	40.0	65.0	Z0684-723
	20704	30.0	52.0	40.0	55.0	"
	20717	13.0	49.0	40.0	90.0	"
	20722	14.0	46.0	40.0	80.0	"
	21666	8.9	60.0	40.0	127.8	Z1664-71
	26822	61.0	105.0	40.0	110.0	Z6819-31
	26828	13.0	32.5	40.0	48.8	"
				Mean	86.0%	
			SD	23.1%		
			cv	0.268		

\* Outlier, excluded from statistics

TABLE E-35. METALS IN SOILS (Continued)

External Controls						
Spike Param.	Prepped Sample #	Unspiked Amount	Spiked Amount	mg Added	% Recovery	Relevant Samples
Fe	EPA-LCS	NA	22400	21800	103	Y2165-90
	Y2167	12100	12200	100	100	"
	Y2179	3090	2680	100	0	"
	Y4850	4500	5900	100	1400	Y4846-54
	Y6710	5650	7020	1500	91	Y6705-14
Hg	EPA-LCS	NA	11.8	12.7	92.9	Y2165-90
Mg	EPA-LCS	NA	118	112	105.4	"
Na	EPA-LCS	NA	50.0	60.5	82.6	"
Ni	EPA-LCS	NA	60.9	71.3	85.4	Y2165-90
	Y2167	47.6	89.1	50.0	83.0	"
	Y2179	12.3	50.9	50.0	77.2	"
	Y4850	22.7	70.4	50.0	95.4	Y4846-54
	Y6710	40.4	95.3	75.0	73.2	Y6705-14
	zoo93	<9.7	80.0	100.0	80.0	20090-94
	20693	41.0	120.0	100.0	79.0	Z0684-723
	Z0704	17.0	97.0	100.0	80.0	"
	20717	14.0	96.0	100.0	82.0	"
	20722	18.0	93.0	100.0	75.0	"
	21666	15.0	110.0	100.0	90.9	Z1664-71
	26822	42.0	64.0	16.0	137.5 **	Z6819-31
	Z6828	27.0	47.7	40.0	51.8	"
				Mean	83.9%	
			SD	19.1%		
			cv	0.228		

\*\* Value greater than two standard deviations from mean

TABLE E-35. METALS IN SOILS (Continued)

External Controls						
Spike Param.	Prepped Sample #	Unspiked Amount	Spiked Amount	mg Added	% Recovery	Relevant Samples
Pb	EPA-LCS	NA	236	267	88.4	Y2165-90
	Y2167	30.5	75.6	50.0	90.2	"
	Y2179	7.4	53.5	50.0	92.2	"
	Y4850	8.3	54.0	50.0	91.4	Y4846-54
	Y6710	45.3	94.5	75.0	65.6	Y6705-14
	zoo93	7.0	121.0	100.0	114.1	Z0090-94
	20693	4.8	100.0	100.0	95.2	Z0684-723
	20704	66.0	130.0	100.0	64.0	"
	20717	4.9	100.0	100.0	95.1	"
	20722	3.0	96.0	100.0	93.0	"
	Z1666	6.5	130.0	200.0	61.8	Z1664-71
	26822	9.4	15.0	2.0	280.0 *	Z6819-31
	26828	4.7	6.3	2.0	80.0	"
				Mean	85.9%	
				SD	15.4%	
			cv	0.180		
V	EPA-LCS	NA'	65.8	73.3	89.8	Y2165-90
	Y2167	30.5	72.7	50.0	84.4	"
	Y2179	19.4	53.6	50.0	68.4	"
	Y4850	19.0	68.8	50.0	99.6	Y4846-54
	Y6710	21.4	93.9	75.0	96.7	Y6705-14
	zoo93	c9.7	90.0	100.0	90.0	Z0090-94
	20693	14.0	110.0	100.0	96.0	Z0684-723
	20704	18.0	100.0	100.0	82.0	"
	20717	14.0	96.0	100.0	82.0	"
	20722	18.0	100.0	100.0	82.0	"
	Z1666	<10.0	95.0	100.0	95.0	Z1664-71
	26822	<10.0	30.1	20.0	150.5 .	Z6819-31
26828	15.0	20.2	20.0	26.0 .	"	
			Mean	87.8%		
			SD	9.1%		
			cv	0.104		

\* Outlier, excluded from statistics

TABLE E-35. METALS IN SOILS (Continued)

External Controls

Spike Param.	Prepped Sample #	Unspiked Amount	Spiked Amount	mg Added	% Recovery	Relevant Samples
Zn	EPA-LCS	NA	187	154	121.4	Y2165-90
	Y2167	30.5	67.1	50.0	73.2	"
	Y2179	12.7	67.1	50.0	108.8	"
	Y4850	13.4	65.1	50.0	103.4	Y4846-54
	Y6710	26.0	107.0	75.0	108.0	Y6705-14
	zoo93	12.4	43.6	100.0	31.2 **	Z0090-94
	20693	13.0	104.0	100.0	91.0	Z0684-723
	20704	60.0	164.0	100.0	104.0	"
	20717	42.0	267.0	100.0	225.0 *	"
	20722	53.0	123.0	100.0	70.0	"
	21666	38.0	120.0	100.0	82.0	Z1664-71
	26822	22.0	28.7	8.0	83.7	Z6819-31
	26828	27.0	30.8	8.0	47.5	"
				Mean	85.4%	
				SD	26.7%	
				cv	0.313	

\* Outlier, excluded from statistics

\*\* Value greater than two standard deviations from mean

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TABLE E-36. METALS IN SOILS

Prepped Duplicate Soil Sample Data  
(units are mg/kg)

Lab Sample #	Value 1	Value 2	% RPD	Relevant Samples (Lab #s)
<u>Parameter: Al</u>				
Y2166	5700	4770	17.77	Y2165-90
Y2173	1750	1860	6.09	"
Y2175	3060	2560	17.79	"
Y2182	3700	3600	2.74	"
Y2189	5620	4380	24.80	"
Y4847	5800	5700	1.74	Y4846-54
Y4852	6700	7000	4.38	"
Y4854	1600	1700	6.06	"
Y5201	3130	2500	22.38	Y5200-04
Y6706	5520	4430	21.91	Y6705-14
Y6713	3270	3170	3.11	"
20092	1100	1800	48.28	Z0090-94
20684	3200	3860	18.70	Z0684-723
20689	2320	1630	34.94	"
20698	2600	2080	22.22	"
20707	2520	2810	10.88	"
20715	6760	6980	3.20	"
21667	1800	1800	0.00	Y1664-71
21667	1800	1800	0.00	"
26820	2600	2120	20.34	Z6819-31
26827	2200	2920	28.13	"
<u>Parameter: As</u>				
Y2166	3.21	2.98	7.43	Y2165-90
Y2173	1.12	0.72	43.48	"
Y2175	1.48	1.47	0.68	"
Y2182	2.52	2.90	14.02	"
Y2189	2.22	1.76	23.12	"
Y4847	2.30	2.60	12.24	Y4846-54
Y4852	5.00	4.50	10.53	"
Y4854	3.20	2.40	28.57	"
Y5201	0.87	0.77	12.20	Y5200-04
Y6706	2.69	2.16	21.86	Y6705-14
Y6713	1.67	1.66	0.60	"
zoo92	<0.64	co.59	0.00	Z0090-94
20684	1.40	2.20	44.44	Z0684-723

TABLE E-36. METALS IN SOILS (Continued)

Prepped Duplicate Soil Sample Data  
(units are mg/kg)

Lab Sample #	Value 1	Value 2	% RPD	Relevant Samples (Lab #s)
<u>Parameter: As (Continued)</u>				
20689	0.96	0.97	1.04	Z0684-723
20698	0.88	1.10	22.22	"
20707	1.50	2.00	28.57	"
Z0715	2.10	2.90	32.00	"
Z1667	0.80	1.00	22.22	Z1664-71
Z6820	1.90	0.80	81.48	Z6819-31
Z6827	4.30	3.20	29.33	"
<u>Parameter: Be</u>				
Y2166	0.906	0.992	9.06	Y2165-90
Y2173	0.315	0.378	18.18	"
Y2175	0.556	0.367	40.95	"
Y2182	0.777	0.596	26.37	"
Y2189	0.771	0.706	8.80	"
Y4847	1.170	0.960	19.72	Y4846-54
Y4852	1.190	1.310	9.60	"
Y4854	0.400	0.590	38.38	"
Y5201	0.380	0.180	71.43	Y5200-04
Y6706	0.710	0.790	10.67	Y6705-14
Y6713	0.580	0.620	6.67	"
zo092	1.100	2.100	62.50	Z0090-94
20684	0.250	0.310	21.43	Z0684-723
20689	0.230	co.190	19.04	"
20698	0.270	0.290	7.14	"
20707	0.490	0.300	48.10	"
20715	0.500	0.410	19.78	"
Z1667	<0.200	co.200	0.00	Z1664-71
Z6820	co.400	co.400	0.00	Z6819-31
Z6827	co.400	co.400	0.00	"

TABLE E-36. METALS IN SOILS (Continued)

Prepped Duplicate Soil Sample Data  
(units are mg/kg)

Lab Sample #	Value 1	Value 2	% RPD	Relevant Samples (Lab #s)
<u>Parameter: Ca</u>				
Y2166	93300	90300	3.27	Y2165-90
Y2173	43600	53900	21.13	"
Y2175	48900	48900	0.00	"
Y2182	93000	135000	36.84	"
Y2189	43000	43600	1.39	"
Y4847	110000	110000	0.00	Y4846-54
Y4852	40000	42000	4.88	"
Y4854	250000	240000	4.08	"
Y5201	36500	31400	15.02	Y5200-04
Y6706	155000	137000	12.33	Y6705-14
Y6713	35200	35500	0.85	"
zoo92	24000	30000	22.22	Z0090-94
Z0684	26000	27000	3.77	Z0684-723
20689	22000	17000	25.64	"
20698	74000	71000	4.14	"
20707	150000	150000	0.00	"
20715	41000	43000	4.76	"
21667	52000	57000	9.17	Z1664-71
26820	170000	170000	0.00	Z6819-31
26827	76000	80000	5.13	"
<u>Parameter: Cd</u>				
Y2166	3.62'	2.78	26.25	Y2165-90
Y2173	1.57	cl.90	9.51	"
Y2175	1.85	1.83	1.09	"
Y2182	2.80	2.98	6.23	"
Y2189	2.50	2.15	15.05	"
Y4847	3.11	2.88	7.68	Y4846-54
Y4852	2.38	2.80	16.22	"
Y4854	2.20	1.98	10.53	"
Y5201	cl.90	cl.80	0.00	Y5200-04
Y6706	cl.77	1.90	7.08	Y6705-14
Y6713	4.62	cl.56	99.03	"
zoo92	cl.90	2.20	14.63	Z0090-94
20684	<2.00	cl.90	0.00	Z0684-723
20689	cl.90	cl.90	0.00	"

TABLE E-36. METALS IN SOILS (Continued)

Prepped Duplicate Soil Sample Data  
(units are mg/kg)

Lab Sample #	Value 1	Value 2	% RPD	Relevant Samples (Lab #s)
<u>Parameter: Cd (Continued)</u>				
20698	cl.90	<2.00	0.00	Z0684-723
20707	2.20	2.30	4.44	"
Z0715	2.80	2.60	7.41	"
21667	2.40	4.10	52.31	Z1664-71
26820	<2.00	<2.00	0.00	Z6819-31
26827	<2.00	<2.00	0.00	"
<u>Parameter: Cr</u>				
Y2166	22.30	20.60	7.93	Y2165-90
Y2173	5.19	13.00	85.87	"
Y2175	14.50	13.40	7.89	"
Y2182	16.50	15.70	4.97	"
Y2189	25.80	20.10	24.84	"
Y4847	114.00	51.50	75.53	Y4846-54
Y4852	27.30	31.40	13.97	"
Y4854	25.40	33.10	26.32	"
Y5201	8.80	9.50	7.65	Y5200-04
Y6706	17.50	10.40	50.90	Y6705-14
Y6713	<4.80	9.52	65.74	"
zo092	8.87	12.10	30.81	Z0090-94
2 0 6 8 4	13.00	20.00	42.42	Z0684-723
20689	17.00	8.30	68.77	"
20698	10.00	9.30	7.25	"
20707	14.00	15.00	6.90	"
20715	34.00	34.00	0.00	"
21667	10.00	9.00	10.53	Z1664-71
26820	13.00	48.50	115.45	Z6819-31
26827	86.00	39.60	73.89	"

TABLE E-36. METALS IN SOILS (Continued)

Prepped Duplicate Soil Sample Data  
(units are mg/kg)

Lab Sample #	Value 1	Value 2	% RPD	Relevant Samples (Lab #s)
<u>Parameter: Fe</u>				
Y2166	7360	6430	13.49	Y2165-90
Y2173	2000	2280	13.08	"
Y2175	3830	3350	13.37	"
Y2182	5140	4630	10.44	"
Y2189	6130	s370	13.22	"
Y4847	7200	7200	0.00	Y4846-54
Y4852	7500	7800	3.92	"
Y4854	2100	2300	9.09	"
Y5201	2880	2230	25.44	Y5200-04
Y6706	7080	5560	24.05	Y6705-14
Y6713	4130	4520	9.02	"
zoo92	1760	2290	26.17	Z0090-94
20684	4000	5290	27.77	Z0684-723
Z0689	2700	2250	18.18	"
20698	2800	2210	23.55	"
20707	4200	4100	2.41	"
20715	8400	8500	1.18	"
Z1667	2000	2200	9.52	Z1664-71
26820	2600	2240	14.88	Z6819-31
26827	4300	4300	0.00	"
<u>Parameter: Hg</u>				
Y2166	<0.036	<0.038	0.00	Y2165-90
Y2173	co.031	co.037	0.00	"
Y2175	0.039	0.060	42.42	"
Y2182	co.040	0.054	29.79	"
Y2189	<0.038	co.031	0.00	"
Y4847	0.040	0.058	36.73	Y4846-54
Y4852	co.040	0.037	7.79	"
Y4854	co.040	0.040	0.00	"
Y5201	<0.038	0.036	5.40	Y5200-04
Y6706	co.035	<0.032	0.00	Y6705-14
Y6713	<0.038	0.031	20.29	"
zoo92	<0.038	co.034	0.00	Z0090-94
Z0684	0.039	0.038	2.60	Z0684-723
20689	<0.038	co.039	0.00	"

TABLE E-36. METALS IN SOILS (Continued)

Prepped Duplicate Soil Sample Data  
(units are mg/kg)

Lab Sample #	Value 1	Value 2	% RPD	Relevant Samples (Lab #s)
<u>Parameter: Hg (Continued)</u>				
20698	<0.038	co.039	0.00	Z0684-723
20707	co.039	<0.037	0.00	"
20715	co.044	<0.039	0.00	"
21667	0.037	0.059	45.83	Z1664-71
26820	<0.036	co.040	0.00	Z6819-31
26827	co.040	<0.038	0.00	"
<u>Parameter: Mg</u>				
Y2166	6145	5380	13.28	Y2165-90
Y2173	4420	5300	18.11	"
Y2175	6910	6420	7.35	"
Y2182	3200	3030	5.46	"
Y2189	6300	5950	5.71	"
Y4847	8300	9200	10.29	Y4846-54
Y4852	8200	8900	8.19	"
Y4854	5800	5800	0.00	"
Y5201	6560	6810	3.74	Y5200-04
Y6706	9170	7050	26.14	Y6705-14
Y6713	5400	4910	9.51	"
zoo92	3200	4400	31.58	Z0090-94
20684	5860	5510	6.16	Z0684-723
20689	3060	1960	43.82	"
20698	6190	5270	16.06	"
20707	2520	2590	2.74	"
20715	8810	9280	5.20	"
21667	5100	4500	12.50	Z1664-71
Z6820	15000	10200	38.10	Z6819-31
26827	6700	9320	32.71	"
<u>Parameter: Na</u>				
Y2166	203	179	12.57	Y2165-90
Y2173	253	282	10.84	"
Y2175	813	801	1.49	"

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TABLE E-36- METALS IN SOILS (Continued)

Prepped Duplicate Soil Sample Data  
(units are mg/kg)

Lab Sample #	Value 1	Value 2	% RPD	Relevant Samples (Lab #s)
<u>Parameter: Na (Continued)</u>				
Y2182	1450	4060	94.74	Y2165-90
Y2189	231	189	20.00	"
Y4847	1000	860	15.05	Y4846-54
Y4852	110	130	16.67	"
Y4854	1600	1600	0.00	"
Y5201	225	184	20.05	Y5200-04
Y6706	878	797	9.67	Y6705-14
Y6713	1890	1703	10.41	"
zoo92	280	390	32.84	Z0090-94
20684	750	1600	72.34	Z0684-723
20689	120	120	0.00	"
20698	690	700	1.44	"
20707	4600	4200	9.09	"
20715	330	360	8.70	"
21667	300	280	6.90	Z1664-71
26820	4700	5100	8.16	Z6819-31
26827	26000	27400	5.24	"
<u>Parameter: Ni</u>				
Y2166	30.6	28.0	8.87	Y2165-90
Y2173	10.5	14.9	34.65	"
Y2175	16.8	20.0	17.39	"
Y2182	20.4	20.0	1.98	"
Y2189	31.4	28.2	10.74	"
Y4847	56.5	53.5	5.45	Y4846-54
Y4852	19.8	37.6	62.02	"
Y4854	25.2	27.1	7.27	"
Y5201	12.3	<9.0	30.99	Y5200-04
Y6706	35.8	27.3	26.94	Y6705-14
Y6713	18.8	22.3	17.03	"
zoo92	<9.4	<8.6	0.00	Z0090-94
20684	19.0	27.0	34.78	Z0684-723
20689	16.0	11.0	37.04	"
Z0698	9.8	11.0	11.54	"
20707	12.0	16.0	28.57	"
20715	40.0	44.0	9.52	"

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TABLE E-36. METALS IN SOILS (Continued)

Prepped Duplicate Soil Sample Data  
(units are mg/kg)

Lab Sample #	Value 1	Value 2	% RPD	Relevant Samples (Lab #s)
<u>Parameter: Ni (Continued)</u>				
21667	19.0	16.0	17.14	Z1664-71
26820	24.0	35.4	38.38	Z6819-31
26827	58.0	36.2	46.28	"
<u>Parameter: Pb</u>				
Y2166	3.55	3.83	7.59	Y2165-90
Y2173	8.65	25.10	97.48	"
Y2175	28.40	23.20	20.16	"
Y2182	14.30	18.80	27.19	"
Y2189	11.40	8.37	30.65	"
Y4847	37.00	31.00	17.65	Y4846-54
Y4852	11.00	13.00	16.67	"
Y4854	2.50	1.80	32.56	"
Y5201	1.50	1.30	14.29	Y5200-04
Y6706	3.40	2.38	35.29	Y6705-14
Y6713	5.54	5.48	1.09	"
zoo92	8.96	12.40	32.21	Z0090-94
20684	9.90	17.00	52.79	Z0684-723
20689	7.20	3.10	79.61	"
20698	11.00	11.00	0.00	"
20707	4.00	4.80	18.18	"
20715	17.00	17.00	0.00	"
21667	5.70	5.50	3.57	Z1664-71
26820	5.40	5.60	3.64	Z6819-31
26827	3.90	4.00	2.53	"
<u>Parameter: V</u>				
Y2166	21.40	17.50	20.05	Y2165-90
Y2173	<7.90	<9.40	0.00	"
Y2175	13.50	11.00	20.41	"
Y2182	16.70	14.10	16.88	"
Y2189	20.40	16.30	22.34	"
Y4847	22.70	22.50	0.88	Y4846-54

TABLE E-36. METALS IN SOILS (Continued)

Prepped Duplicate Soil Sample Data  
(units are mg/kg)

Lab Sample #	Value 1	Value 2	% RPD	Relevant Samples (Lab #s)
<u>Parameter: V (Continued)</u>				
Y4852	31.70	31.40	0.95	Y4846-54
Y4854	18.80	17.60	6.59	"
Y5201	11.00	9.55	14.11	Y5200-04
Y6706	34.20	25.20	30.30	Y6705-14
Y6713	22.90	21.10	8.18	"
zoo92	<9.40	9.30	1.07	Z0090-94
Z0684	16.00	20.70	25.61	Z0684-723
20689	10.00	6.80	38.10	"
20698	12.00	10.20	16.22	"
20707	15.00	16.00	6.45	"
20715	29.00	30.00	3.39	"
Z1667	<10.00	<10.00	0.00	Z1664-71
26820	14.00	11.10	23.11	Z6819-31
26827	21.00	24.90	16.99	"
<u>Parameter: Zn</u>				
Y2166	24.10	15.10	45.92	Y2165-90
Y2173	7.55	10.20	29.86	"
Y2175	45.60	43.20	5.41	"
Y2182	14.60	15.50	5.98	"
Y2189	27.70	30.70	10.27	"
Y4847	109.00	118.00	7.93	Y4846-54
Y4852	18.60	31.20	50.60	"
Y4854	<7.00	<6.90	0.00	"
Y5201	6.73	6.13	9.33	Y5200-04
Y6706	15.40	11.40	29.85	Y6705-14
Y6713	8.65	11.10	24.81	"
zoo92	8.68	12.60	36.84	Z0090-94
Z0684	32.00	20.00	46.15	Z0684-723
20689	<9.60	<9.70	0.00	"
20698	11.00	<9.80	11.50	"
20707	58.00	44.70	25.90	"
20715	50.00	46.40	7.47	"
Z1667	30.00	24.00	22.22	Z1664-71
26820	24.00	24.20	0.83	Z6819-31
26827	21.00	23.80	12.50	"

TABLE E-37. METALS IN SOILS

Instrument Duplicate Analysis Data  
(units are mg/L)

Lab Sample #	Value 1	Value 2	% RPD	Relevant Samples (Lab #s)
<u>Parameter: Al</u>				
Y2165	30.2	30.9	2.26	Y2165-90
Y2177	13.0	12.9	0.46	"
Y2183	14.0	14.1	0.50	"
Y4849	21.4	21.3	0.33	Y4846-54
Y4854	7.9	7.9	0.51	"
Y5202	10.1	10.2	0.99	Y5200-04
Y6708	22.6	22.5	0.44	Y6705-14
Y6714	21.6	21.9	1.38	"
zoo94	6.8	6.7	1.48	Z0090-94
20690	18.3	18.2	0.05	Z0684-0723
20699	27.7	28.4	2.46	"
Z0711	15.7	15.8	0.51	"
20720	23.9	24.2	1.08	"
21668	12.3	12.2	0.82	'21664-71
26821	10.2	10.1	0.99	Z6819-31
26831	8.3	8.3	0.00	"
<u>Parameter; As</u>				
Y2165	0.0203	0.0204	0.49	Y2165-90
Y2167	0.0189	0.0212	11.47	"
Y2183	0.0157	0.0175	10.84	"
Y2188	0.0122	0.0131	7.11	"
Y4853	0.0040	0.0041	2.47	Y4846-54
Y5200	0.0065	0.0058	11.38	Y5200-04
Y5202	0.0035	0.0033	5.88	"
Y6710	0.0114	0.0104	9.17	Y6705-14
Z0090	0.0052	0.0059	12.61	Z0090-94
20691	0.0080	0.0074	7.79	Z0684-0723
20701	0.0154	0.0163	5.68	"
20713	0.0110	0.0102	7.55	"
20722	0.0122	0.0131	7.11	"
21666	0.0045	0.0045	0.00	Z1664-71
26821	0.0080	0.0073	9.15	Z6819-31
26829	0.0132	0.0158	17.93	"

TABLE E-37. METALS IN SOILS (Continued)

Instrument Duplicate Analysis Data  
(units are mg/L)

Lab-Sample #	Value 1	Value 2	% RPD	Relevant Samples (Lab #s)
<u>Parameter: Be</u>				
Y2165	0.005	0.005	0.00	Y2165-90
Y2177	0.002	0.002	0.00	"
Y2188	0.005	0.005	0.00	"
Y2190	0.080	0.081	1.24	"
Y4848	0.003	0.003	0.00	Y4846-54
Y4853	0.002	0.002	0.00	"
Y5201	0.002	0.002	0.00	Y5200-04
Y6708	0.003	0.003	0.00	Y6705-14
Y6713	0.003	0.003	0.00	"
20093	0.006	0.006	0.00	Z0090-94
Z0691	0.002	0.002	0.00	Z0684-0723
20703	0.004	0.004	0.00	"
20715	0.003	0.002	8.33	"
20721	0.003	0.003	3.77	"
Z1671	0.127	0.125	1.59	Z1664-71
26830	0.004	0.004	0.00	Z6819-31
26830	0.003	0.003	0.00	"
<u>Parameter: Ca</u>				
Y2165	336.4	348.9	3.65	Y2165-90
Y2177	275.2	267.7	2.76	"
Y2186	183.7	184.8	0.60	"
Y4850	122.1	121.7	0.33	Y4846-54
Y5200	29.3	30.2	3.03	Y5200-04
Y6713	183.0	178.0	2.77	Y6705-14
zoo94	75.6	73.9	2.27	Z0090-94
20684	141.0	146.0	3.48	Z0684-0723
20689	115.0	115.0	0.00	"
20706	co.050	co.050	0.00	"
20722	9.8	10.8	9.91	"
Z1671	32.0	32.7	2.16	Z1664-71
26821	15.0	15.2	1.32	Z6819-31
26825	37.7	38.4	1.84	"

TABLE E-37. METALS IN SOILS (Continued)

Instrument Duplicate Analysis Data  
(units are mg/L)

Lab Sample #	Value 1	Value 2	% RPD	Relevant Samples (Lab #s)
<u>Parameter: Cd</u>				
Y2165	0.016	0.018	11.76	Y2165-90
Y2179	0.010	0.010	0.00	"
Y2189	0.013	0.015	14.29	"
Y4852	0.012	0.011	8.70	Y4846-54
Y5203	0.010	0.010	0.00	Y5200-04
Y6713	0.024	0.025	4.08	Y6705-14
zoo93	0.050	0.049	2.02	Z0090-94
Z0684	0.010	<0.010	0.00	Z0684-0723
20696	0.012	0.011	3.51	"
20710	0.012	0.012	2.49	"
Z1670	0.022	0.022	0.00	Z1664-71
Z6821	<0.010	<0.010	0.00	Z6819-31
Z6828	<0.010	<0.010	0.00	"
<u>Parameter: Cr</u>				
Y2165	0.113	0.111	1.79	Y2165-90
Y2178	0.045	0.049	8.51	"
Y2181	0.061	0.070	13.74	"
Y4849	0.101	0.103	1.96	Y4846-54
Y4854	0.127	0.132	3.86	"
Y5201	0.046	0.053	14.14	Y5200-04
Y6705	0.178	0.180	1.12	Y6705-14
zoo91	0.091	0.105	14.29	Z0090-94
Z0684	0.093	0.096	3.40	Z0684-0723
Z0696	0.114	0.115	0.61	"
20710	0.096	0.097	1.04	"
20719	0.076	0.080	5.39	"
Z1670	0.075	0.076	1.32	Z1664-71
Z6821	0.058	0.056	3.51	Z6819-31
Z6828	0.066	0.064	3.08	"

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TABLE E-37. METALS IN SOILS (Continued)

Instrument Duplicate Analysis Data  
(units are mg/L)

Lab Sample #	Value 1	Value 2	% RPD	Relevant Samples (Lab #s)
<u>Parameter: Fe</u>				
Y2165	37.60	38.65	2.75	Y2165-90
Y2178	12.93	12.78	1.17	"
Y2182	23.80	23.51	1.23	"
Y4850	23.21	23.25	0.17	Y4846-54
Y5202	10.24	10.13	1.08	Y5200-04
Y6714	29.40	28.60	2.76	Y6705-14
zoo91	15.90	15.00	5.83	Z0090-94
Z0688	14.43	14.42	0.07	Z0684-0723
20701	27.35	27.62	0.98	"
Z0708	28.64	28.98	1.18	"
20721	40.89	41.48	1.43	"
21670	15.30	15.30	0.00	Z1664-71
Z6821	10.80	10.70	0.93	Z6819-31
Z6828	16.50	16.10	2.45	"
<u>Parameter: Hg</u>				
Y2167	0.0002	0.0002	0.00	Y2165-90
Y2176	<0.0002	<0.0002	0.00	"
Y4847	0.0002	0.0002	0.00	Y4846-54
Y4852	<0.0002	<0.0002	0.00	"
Y5202	0.0002	0.0002	0.00	Y5200-04
Y6705	0.0003	0.0003	0.00	Y6705-14
Y6711	0.0002	0.0002	0.00	"
Z0090	<0.0002	<0.0002	0.00	Z0090-94
Z0684	0.0005	0.0004	22.22	Z0684-0723
20700	0.0002	<0.0002	0.00	"
20709	<0.0002	<0.0002	0.00	"
20719	~0.0002	<0.0002	0.00	"
21665	0.0003	0.0003	0.00	Z1664-71
Z6820	<0.0002	<0.0002	0.00	Z6819-31
Z6825	<0.0002	<0.0002	0.00	"

TABLE E-37. METALS IN SOILS (Continued)

Instrument Duplicate Analysis Data  
(units are mg/L)

Lab Sample #	Value 1	Value 2	% RPD	Relevant Samples (Lab #s)
<u>Parameter: Mg</u>				
Y2166	33.91	33.77	0.41	Y2165-90
Y2173	28.13	27.80	1.18	"
Y2186	23.95	24.32	1.53	"
Y4851	16.54	16.54	0.00	Y4846-54
Y5200	9.27	9.27	0.00	Y5200-04
Y6713	28.10	28.00	0.36	Y6705-14
zoo94	21.40	21.30	0.47	Z0090-94
Z0684	30.12	31.58	4.73	Z0684-0723
20700	23.54	23.45	0.38	"
20706	<0.25	<0.25	0.00	"
20714	38.40	37.89	1.34	"
21671	18.20	18.10	0.55	Z1664-71
26821	30.50	30.40	0.33	Z6819-31
Z6831	5.08	5.02	1.19	"
<u>Parameter: Na</u>				
Y2166	1.12	1.10	1.89	Y2165-90
Y2173	1.61	1.61	0.12	"
Y4852	0.76	0.80	5.12	Y4846-54
Y5204	1.58	1.57	0.57	Y5200-04
Y6714	6.99	6.66	4.84	Y6705-14
zoo92	1.51	1.54	1.97	Z0090-94
20690	1.01	1.13	11.21	Z0684-0723
20696	3.96	3.45	13.77	"
20710	35.97	33.30	7.71	"
20721	6.96	6.81	2.18	"
21664	3.00	3.20	6.45	Z1664-71
Z6819	16.50	16.60	0.60	Z6819-31
Z6831	17.60	17.90	1.69	"

TABLE E-37. METALS IN SOILS (Continued)

Instrument Duplicate Analysis Data  
(units are mg/L)

Lab Sample #	Value 1	Value 2	% RPD	Relevant Samples (Lab #s)
<u>Parameter: Ni</u>				
Y2169	0.238	0.246	3.31	Y2165-90
Y2173	0.067	0.064	4.58	"
Y2181	0.112	0.117	4.37	"
Y2187	0.150	0.153	1.98	"
Y4848	0.085	0.088	3.47	Y4846-54
Y4853	0.054	0.056	3.64	"
Y5204	0.348	0.330	5.31	Y5200-04
Y6713	0.098	0.100	2.02	Y6705-14
zoo91	0.082	0.086	4.76	Z0090-94
20692	0.146	0.140	4.20	Z0684-0723
20696	0.166	0.173	4.13	"
20714	0.170	0.171	0.59	"
20720	0.132	0.142	7.30	"
21670	0.111	0.101	9.43	Z1664-71
Z6821	0.052	0.061	15.93	Z6819-31
26828	0.137	0.134	2.21	"
<u>Parameter: Pb (flame)</u>				
Y2166	0.217	0.200	8.15	Y2165-90
Y2171	0.209	0.224	6.93	"
Y2190	1.339	1.332	0.52	"
<u>Parameter: Pb (furnace)</u>				
Y2174	0.0585	0.0670	13.55	Y2165-90
Y2182	0.0722	0.0632	13.29	"
Y2189	0.0591	0.0608	2.84	"
Y4848	0.0340	0.0354	4.03	Y4846-54
Y5201	0.0039	0.0037	5.26	Y5200-04
Y5204	0.0016	0.0018	11.76	"
Y6707	0.0202	0.0197	2.51	Y6705-14
Y6713	0.0288	0.0262	9.45	"
zoo92	0.0475	0.0473	0.42	Z0090-94
Z0686	0.0343	0.0340	0.88	Z0684-0723
Z0698	0.0279	0.0286	2.48	"
20707	0.0203	0.0217	6.67	"
20717	0.0249	0.0253	1.59	"
21670	0.0476	0.0489	2.69	Z1664-71
Z6821	0.0215	0.0225	4.55	Z6819-31
26829	0.0231	0.0258	11.04	"

TABLE E-37. METALS IN SOILS (Continued)

Instrument Duplicate Analysis Data  
(units are mg/L)

Lab Sample #	Value 1	Value 2	% RPD	Relevant Samples (Lab #s)
<u>Parameter: V</u>				
Y2165	0.129	0.138	6.74	Y2165-90
Y2177	0.059	0.059	0.00	"
Y2190	0.054	0.058	7.14	"
Y4849	0.073	0.085	15.19	Y4846-54
Y5204	0.060	0.061	1.65	Y5200-04
Y6709	0.100	0.097	3.05	Y6705-14
Y6714	0.149	0.139	6.94	"
20091	0.059	0.059	0.00	Z0090-94
20684	0.109	0.107	1.85	20684-0723
20700	0.053	0.050	5.83	"
20712	0.106	0.106	0.00	"
20721	0.184	0.187	1.62	"
21670	0.068	0.065	4.51	Z1664-71
26820	0.076	0.078	2.60	Z6819-31
26830	0.121	0.118	2.51	"
<u>Parameter: Zn</u>				
Y2165	0.123	0.122	0.82	Y2165-90
Y2179	0.086	0.084	2.35	"
Y2189	0.164	0.167	1.81	"
Y4852	0.129	0.127	1.56	Y4846-54
Y5203	0.042	0.041	2.41	Y5200-04
Y6705	0.102	0.103	0.98	Y6705-14
zoo91	0.093	0.111	17.65	Z0090-94
20689	0.091	0.088	3.35	Z0684-0723
20699	0.497	0.492	1.01	"
20710	0.233	0.231	0.86	"
20721	0.482	0.481	0.21	"
21670	0.397	0.426	7.05	Z1664-71
26821	0.068	0.068	0.00	Z6819-31
26828	0.135	0.126	6.90	"

TABLE E-38. METALS IN SOILS

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: Al</u>				
Y2165	30.2	39.4	96.2	Y2165-90
Y2177	13.0	17.8	97.4	"
Y2183	14.0	18.9	98.3	"
Y4849	21.4	31.5	103.8	Y4846-54
Y4854	7.9	18.2	103.9	"
Y5202	10.1	14.9	97.5	Y5200-04
Y6708	22.6	32.9	106.3	Y6705-14
Y6714	21.6	31.0	97.1	"
zoo94	6.8	11.2	88.7 *	Z0090-94
20684	21.0	30.4	96.7	Z0684-0723
20699	27.7	37.4	100.3	"
20711	15.7	25.2	97.7	"
20720	23.9	33.2	96.4	"
21667	9.4	13.2	106.8	Z1664-71
26821	10.2	14.9	95.5	Z6819-31
26831	8.3	12.9	92.9.	"
		Mean	98.5 %	
		SD	4.8 %	
		cv	0.049	
<u>Parameter: As</u>				
Y2165	0.0203	0.0289	88.9	Y2165-90
Y2167	0.0189	0.0294	107.9	"
Y2183	0.0157	0.0354	102.0	"
Y2189	0.0115	0.0301	96.0	"
Y4846	0.0026	0.0129	104.3	Y4846-54
Y5201	0.0045	0.0145	101.5	Y5200-04
Y5203	0.0043	0.0140	98.4	"
Y6713	0.0087	0.0177	91.8	Y6705-14
zoo91	0.0068	0.0158	91.6	Z0090-94
20693	0.0063	0.0168	106.7	Z0684-0723
Z0705	-0.0148	0.0235	89.4	"

\* Value greater than two standard deviations from mean

TABLE E-38. METALS IN SOILS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: As (Continued)</u>				
20712	0.0170	0.0258	90.6	Z0684-0723
20722	0.0122	0.0215	95.2	"
21670	0.0068	0.0163	96.6	Z1664-71
26821	0.0080	0.0176	97.8	Z6819-31
26831	0.0091	0.0201	112.0	"
		Mean	98.2 %	
		SD	7.0 %	
		CV	0.072	
<u>Parameter: Be</u>				
Y2165	0.00s	0.014	91.4	Y2165-90
Y2177	0.002	0.011	91.1	"
Y2188	0.005	0.014	91.4	"
Y4848	0.003	0.012	91.2	Y4846-54
Y4853	0.002	0.011	91.1	"
Y5201	0.002	0.011	91.1	Y5200-04
Y6708	0.003	0.012	91.2	Y6705-14
Y6713	0.003	0.011	81.1	"
zoo93	0.006	0.015	93.5	Z0090-94
Z0686	0.002	0.011	90.1	Z0684-0723
20697	0.002	0.010	78.0 *	"
20702	0.003	0.011	87.1	"
20710	0.002	0.011	89.1	"
20717	0.001	0.011	97.1	"
21665	0.001	0.009	90.9	Z1664-71
21671	0.127	0.222	96.5	"
26820	0.004	0.015	111.5	Z6819-31
26830	0,003	0.012	91.2	"
		Mean	-91.4 %	
		SD	6.8 %	
		cv	0.074	

\* Value greater than two standard deviations from mean

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TABLE E-38. METALS IN SOILS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: Ca</u>				
Y5200	29.3	39.2	102.9	Y5200-04
Y6713	183.0	233.0	102.3	Y6705-14
20689	115.0	156.0	85.1	Z0684-0723
20706	co.1	9.6	97.4	"
20722	9.8	18.8	92.1	"
21671	32.0	40.9	93.1	Z1664-71
26821	15.0	24.6	98.5	Z6819-31
26825	37.7	47.9	106.8	"
		Mean	97.3 %	
		SD	7.0 %	
		cv	0.072	
<u>Parameter: Cd</u>				
Y2165	0.016	0.118	103.2	Y2165-90
Y2179	0.010	0,105	96.1	"
Y2189	0.013	0.118	106.2	"
Y4852	0.012	0,117	106.2	Y4846-54
Y6713	0.024	0.116	93.2	Y6705-14
zoo93	0.050	0.145	96.5	Z0090-94
20687	<0.010	0.091	91.4	Z0684-0723
20701	0.011	0.088	86.6	"
20711	<0.010	0.093	102.5	"
21670	0.022	0.203	90.7	Z1664-71
26821	<0.010	0.481	96.7	Z6819-31
26828	<0.010	0.493	99.1	"
		Mean	97.4 %	
		SD	6.3 %	
		cv	0.065	

TABLE E-38. METALS IN SOILS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: Cr</u>				
Y2165	0.113	0.294	90.8	Y2165-90
Y2178	0.045	0.244	99.7	"
Y2181	0.061	0.280	109.8	"
Y4849	0.101	0.297	98.3	Y4846-54
Y4854	0.127	0.307	90.3	"
Y5201	0.046	0.256	105.3	Y5200-04
Y6705	0.178	0.268	92.7	Y6705-14
Z0091	0.091	0.186	96.9	Z0090-94
20687	0.071	0.159	88.9	Z0684-0723
20701	0.093	0.165	89.1	"
20711	0.077	0.157	95.9	"
21670	0.075	0.269	97.3	Z1664-71
26821	0.058	0.513	91.5	Z6819-31
26828	0.066	0.536	94.5	"
		Mean	95.8 %	
		SD	6.1 %	
		cv	0.064	
<u>Parameter: Fe</u>				
Y2165	37.60	48.18	110.6 *	Y2165-90
Y2178	12.93	17.46	135.0 *	"
Y2182	23.80	32.55	136.8 *	"
Y4850	23.21	32.49	96.1	Y4846-54
Y5202	10.24	19.80	97.6	Y5200-04
Y6714	29.40	39.00	99.9	Y6705-14
zoo91	15.90	20.00	84.0	Z0090-94
20688	14.43	23.91	97.2	Z0684-0723
20700	12.14	21.03	91.0	"
20708	28.64	37.84	95.8	"
20720	26.63	36.30	100.3	"

\* Value greater than two standard deviations from mean

TABLE E-38. METALS IN SOILS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: Fe (Continued)</u>				
Z1665	20.30	28.20	81.9	Z1664-71
Z1669	15.32	24.38	93.1	"
Z6821	10.80	15.30	91.5	Z6819-31
Z6828	16.50	25.50	92.6	"
		Mean	94.3 %	
		SD	6.9 %	
		cv	0.073	
<u>Parameter: Hg</u>				
Y2166	<0.0002	0.0011	105.0	Y2165-90
Y2173	<0.0002	0.0011	105.0	"
Y4846	0.0002	0.0011	95.5	Y4846-54
Y4848	0.0002	0.0012	101.0	Y4846-54
Y5200	0.0003	0.0014	106.0	Y5200-04
Y6705	0.0003	0.0013	96.5	Y6705-14
Y6711	0.0002	0.0013	105.5	"
Z0091	<0.0002	0.0013	110.5	Z0090-94
Z0093	0.0002	0.0013	94.5	"
Z0700	~0.0002	0.0013	110.5	Z0684-0723
Z0714	<0.0002	0.0013	110.5	"
Z0721	<0.0002	0.0013	110.5	"
Z1664	0.0005	0.0017	104.5	Z1664-71
Z6820	<0.0002	0.0023	96.6	Z6819-31
		Mean	103.7 %	
		SD	5.9 %	
		CV	0.057	
<u>Parameter: Mg</u>				
Y2166	33.91	43.72	102.5	Y2165-90
Y2173	28.13	37.08	93.2	"
Y2186	23.95	34.20	105.9	"

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TABLE E-38. METALS IN SOILS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
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Parameter: Mg (Continued)

Y4851	16.54	25.55	92.7	Y4846-54
Y5200	9.27	19.10	100.2	Y5200-04
Y6713	28.10	37.90	101.8	Y6705-14
20094	21.40	26.00	94.6	Z0090-94
20687	23.18	32.04	91.8	Z0684-0723
20700	23.54	31.84	86.2	"
Z0711	18.45	26.65	84.7	"
20716	25.79	34.03	85.8	"
20722	18.27	26.00	79.9	"
Z1671	18.20	28.50	105.9	Z1664-71
26821	30.50	47.90	91.8	Z6819-31
26831	5.10	7.24	108.7	"

Mean 95.0 %  
SD 8.8 %  
cv 0.092

Parameter: Na

Y2166	1.12	2.22	111.8	Y2165-90
Y2173	1.61	2.58	99.2	"
Y2188	1.40	2.37	99.9	"
Y4852	0.76	1.84	109.5	Y4846-54
Y5200	2.69	3.66	104.5	Y5200-04
Y6714	6.99	16.00	91.7	Y6705-14
zoo92	1.51	2.55	106.6	Z0090-94
20690	1.01	1.48	97.0	Z0684-0723
20701	1.82	2.91	114.8	"
20708	7.33	10.96	101.7	"
20721	6.96	10.58	101.1	"
Z1667	1.62	2.64	104.1	Z1664-71
26819	16.50	27.20	109.7	Z6819-31
26831	17.60	28.30	109.8	"

Mean 104.4 %  
SD 6.4 %  
CV 0.061

TABLE E-38. METALS IN SOILS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: Ni</u>				
Y2167	0.243	0.408	86.6	Y2165-90
Y2173	0.067	0.231	84.3	"
Y2181	0.112	0.280	86.8	"
Y2188	0.215	0.363	77.6	"
Y4848	0.085	0.552	94.0	Y4846-54
Y4853	0.054	0.529	95.5	"
Y5204	0.348	0.868	104.9	Y5200-04
Y6713	0.098	0.204	108.0	Y6705-14
zoo91	0.082	0.179	97.9	Z0090-94
20686	0.111	0.207	98.1	Z0684-0723
20696	0.166	0.273	109.7	"
20714	0.170	0.245	77.5	"
20720	0.137	0.227	92.3	"
21670	0.111	0.368	128.9 *	Z1664-71
26821	0.052	0.514	92.9	Z6819-31
26828	0.137	0.632	99.6	"
		Mean	95.9 %	
		SD	13.0 %	
		cv	0.135	
<u>Parameter: Pb (flame)</u>				
Y2166	0.217	2.034	91.1	Y2165-90
Y2171	0.209	2.067	93.1	"
Y2190	1.339	3.403	103.5	"
		Mean	95.9%	
		SD	6.6%	
		CV	0.069	

\* Value greater than two standard deviations from mean

TABLE E-38. METALS IN SOILS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: Pb (furnace)</u>				
Y2168	0.0247	0.0336	92.4	Y2165-90
Y2173	0.0550	0.0736	100.4	"
Y2180	0.0314	0.0514	105.1	"
Y4849	0.0300	0.0400	104.0	Y4846-54
Y5200	0.0020	0.0111	92.1	Y5200-04
Y5202	0.0024	0.0115	92.2	"
Y5204	0.0016	0.0115	100.2	"
Y6708	0.0010	0.0100	101.0	Y6705-14
zoo92	0.0475	0.0644	90.9	Z0090-94
20686	0.0343	0.0522	94.7	20684-0723
Z0698	0.0279	0.0367	91.7	"
20707	0.0205	0.0304	102.0	"
20717	0.0249	0.0342	96.4	"
21670	0.0476	0.0656	96.6	Z1664-71
26821	0.0215	0.0306	94.1	Z6819-31
26831	0.0389	0.0476	91.8	"
		Mean	96.6 %	
		SD	4.8 %	
		CV	0.050	
<u>Parameter: V</u>				
Y2165	0.129	0.598	94.4	Y2165-90
Y2177	0.059	0.540	96.7	"
Y2190	0.054	0.515	92.7	"
Y4849	0.073	0.567	99.4	Y4846-54
Y5204	0.060	0.527	93.9	Y5200-04
Y6709	0.100	0.553	91.2	Y6705-14
Y6714	0.149	0.653	101.5	"
zoo91	0.059	0.534	95.5	20090-94
20684	0.109	0.211	104.0	Z0684-0723
20701	0.106	0.206	101.8	"
20712	0.106	0.202	98.5	"
20720	0.112	0.210	100.0	"

TABLE E-38. METALS IN SOILS (Continued)

Post-Digested Instrument Spike Data  
(units are mg/L)

Lab Sample#	Unspiked Value	Spiked Value	% Recovery	Relevant Samples (Lab #s)
<u>Parameter: V (Continued)</u>				
21670	0.068	0.245	88.8	Z1664-71
26820	0.076	0.605	106.4 *	Z6819-31
26830	0.121	0.565	89.4	"
		Mean	96.9 %	
		SD	5.3 %	
		cv	0.055	
<u>Parameter: Zn</u>				
Y2165	0.123	0.220	99.2	Y2165-90
Y2179	0.086	0.176	91.8	"
Y2189	0.164	0.266	104.7	"
Y4852	0.129	0.227	100.3	Y4846-54
Y5204	0.074	0.165	92.7	Y5200-04
Y6705	0.102	0.193	92.9	Y6705-14
zoo91	0.093	0.184	92.8	Z0090-94
20685	0.231	0.324	96.3	Z0684-0723
20696	0.409	0.579	90.7	"
Z0717	0.286	0.370	88.1	"
20720	0.305	0.399	97.7	"
21670	0.397	0.594	99.1	Z1664-71
26821	0.068	0.539	94.7	Z6819-31
26828	0.135	0.596	92.8	"
		Mean	95.3 %	
		SD	4.5 %	
		cv	0.047	

\* value greater than two standard deviations from mean

ANNEX

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REPLY TO  
ATTENTION OF

HSHB-ML-O

**FINAL REPORT**  
**KUWAIT OIL, FIRE HEALTH RISK ASSESSMENT**  
**NO. 39-26-L192-91**  
**5 MAY - 3 DECEMBER 1991**

**APPENDIX E**

**PHASE 2**  
**METHODOLOGIES, ANALYTICAL RESULTS, AND**  
**QUALITY ASSURANCE BASED ON**  
**RETURN TRIP OF OCTOBER-NOVEMBER 1993**

**1. PURPOSE.** This appendix details the methodologies used in analyses of samples taken from October-November 1993 in support of the **Final** Kuwait Health Risk Assessment. It summarizes the **analytical** results and the quality assurance procedures employed in support of these analyses. This assessment was limited in scope and of short duration in comparison to the Interim Kuwait Health Risk Assessment (May-November 1991). It focused on **data gaps identified** in that report.

**2. METHODOLOGIES USED FOR SAMPLING AND ANALYSIS.** Methods employed during this phase of the health risk assessment included U.S. Environmental Protection Agency (EPA) ambient air methods:

- TO-1 for the determination of volatile organic compounds (VOCs) in ambient air using Tenax adsorption and gas chromatographic/mass spectrometry (GC/MS) (reference 1);
- TO-9 for the determination of polychlorinated dibenzo-p-dioxins (PCDDs) in ambient air using high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) (reference 2); and
- TO-13 for the determination of benzo(a)pyrene [b(a)p] and other polynuclear aromatic hydrocarbons (PAHs) in ambient air using GC and high performance liquid chromatographic (HPLC) analysis (reference 3).

High volume samplers were used to collect airborne particulates which were subsequently analyzed for selected metals by a variety of EPA procedures (references 4-9). Soil samples were collected for analysis of 14 metals by a variety of approved EPA procedures (references

9-12). Soil samples were screened in the field for the presence of hexavalent chromium by a colorimetric procedure (reference 13). Water soluble hexavalent chromium salts were selectively extracted onto an organotin-modified solid phase extraction cartridge in the field and brought back for laboratory analysis (reference 14). Analytical procedures and sampling media employed are described below.

a. EPA Ambient Air Methods for Organic Compounds.

(1) EPA Method TO-1 was used to analyze a selected group of VOCs (Annex E-2). Low volume pumps were used to draw air through glass tubes filled with 60/80 mesh Tenax (2,6 diphenylphenylene oxide) polymer. Between 10 to 20 liters of air is the recommended sampling volume. Certain VOCs such as benzene, toluene, and xylene are adsorbed onto the Tenax, while other highly volatile organic compounds as well as atmospheric gases pass through the sorbent. The tubes were prepared at the U.S. Army Environmental Hygiene Agency (USAEHA), checked for contamination and sealed with gas-tight fittings. The sampling train consisted of a primary tube followed by a backup tube. The purpose of the backup tube was to monitor breakthrough of analytes not retained on the primary tube. For analysis,\* the tube is placed in a heated chamber and purged with an inert gas. The inert gas transfers the VOCs from the tube onto a cold trap and subsequently onto the front of the GC column which is held at room temperature (approximately 30 °C). The GC column temperature is then increased and the components eluting from the column are identified and quantified by mass spectrometry.

(2) EPA Method TO-9 was used for the analysis of dioxin in ambient air (Annex E-3). High volume samplers were used to draw air through a cartridge filled with a polyurethane foam (PUF) filter and equipped with a prefilter used to collect particulate matter. It is recommended that at least 325 cubic meters of air be drawn through the filter. After collection, the filters were sealed and sent back for laboratory analysis. The prefilter and PUF adsorbent cartridge were extracted together, thereby ensuring that any dioxin vapors or dioxin trapped on particulate material would be extracted and available for quantification. The extracts were analyzed by an HRGC/HRMS method of analysis.

(3) EPA Method TO-13 was used for the determination of PAHs (Annex E-4) in ambient air. High volume samplers were used to draw air through XAD collection cartridges. It is recommended that at least 325 cubic meters of air be drawn through the cartridges. XAD-2 is an organic resin used to collect PAHs. The resin was removed from the cartridges and Soxhlet extracted with methylene chloride to remove the analytes of interest. The extract was concentrated and analyzed by a GC/MS method of analysis.

**b. Inorganic Methods.**

(1) **Field Screening for Hexavalent Chromium.** Soil samples were screened in the field for the presence of hexavalent chromium by a rapid field screening procedure (Annex E-5). Approximately 20 grams of soil was mixed with an alkaline solution of 40 milliliter (mL) of ASTM Type II water and the contents of an extractant pillow from the test kit. After agitation, the emulsified soil sample was filtered. Two 10 mL aliquots were taken and diluted to 25 mL. The first aliquot was treated with a color developing reagent, while the second aliquot served as the blank. The test kit's primary active ingredient is diphenylcarbazide. In the presence of hexavalent chromium, a redviolet color is produced. The color produced was read by a color viewer to determine the amount of hexavalent chromium present. This method is specific only for the water soluble salts of hexavalent chromium, although other metal salts such as molybdenum, mercury or vanadium salts can cause interferences in quantitation of the hexavalent chromium.

(2) **Soil Samples for Metal Analyses.** Soil samples were digested using a procedure employing nitric acid, hydrogen peroxide and hydrochloric acid (Annex E-6). The extracts were analyzed for 14 selected metals by a variety of EPA-approved methods including SW 846 Methods 6010, 7060, and 7131 (Annexes E-7, E-8, and E-9, respectively). In addition, EPA Method 245.5 (Annex E-10) was also used.

(3) **High Volume Samplers for Metal Analysis.** High volume samplers were used to collect atmospheric dust and particulate material. Atmospheric sampling was generally conducted for a 24-hour period at a collection rate of approximately 1.5 cubic meters per minute. A portion of the filter was digested with hot nitric acid to put the metals into solution (Annex E-11). The filters were analyzed for 14 selected metals using a variety of EPA-approved methodologies, including 200.7, 206.2, 213.2, 245.1, and 239.2 (Annexes E-12, E-13, E-14, E-15, and E-16, respectively).

(4) **Hexavalent Chromium in Soil (Annex E-17).** Approximately 20 grams of soil was mixed with 50 mL of deionized water and allowed to stand for 30 minutes. The extract was filtered and drawn through a C-18 solid phase extraction cartridge (SPE) which had been modified with tributyl tin. Only water soluble hexavalent chromium salts were trapped on the C-18 cartridge. The cartridge was capped and shipped for laboratory analysis of the total chromium content of the cartridge. This now represented the amount of hexavalent chromium in the soil at the time of stabilization on the SPE cartridge.

### 3. SUMMARY OF ANALYTICAL RESULTS.

#### a. EPA Ambient Air Methods for Organic Compounds.

(1) EPA Method TO-1. Most of the samples tested contained measurable amounts of the seven target analytes. The limit of quantitation for the target analytes is 10 micrograms per sample. The highest concentrations ranged up to 33 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ) of ambient air. This was the concentration of meta/para xylene in sample number R3787. In addition to the seven target analytes which were quantitated, an estimate was made of the total VOCs by comparing the residual areas of the peaks in the chromatograms (total peak areas less internal standards and surrogates) relative to toluene-d8. Values for total VOCs ranged from nondetect to  $854 \mu\text{g}/\text{m}^3$  (R3757). Two nontarget compounds were detected at very high levels in several of the samples and at somewhat lower concentrations in other samples (methyl methacrylate and trichloroethylene). Results of the TO-1 analyses are given in Annex E-18.

(2) EPA Method TO-9. To date, no analytical data has been received for the TO-9 analyses. Ten samples were sent to the EPA Stennis Space Center laboratory at Bay St. Louis, Mississippi for analysis while 11 samples were sent to Battelle Laboratories of Columbus, Ohio for analysis.

(3) EPA Method TO-13. Naphthalene and 2-methylnaphthalene were the only target PAHs detected above the quantitation limits of  $10 \mu\text{g}/\text{sample}$ . Their concentration ranged up to  $64 \mu\text{g}/\text{sample}$  of naphthalene in sample R3709 and up to 25 micrograms/sample of 2-methylnaphthalene in sample R3712. Several of the samples contained low levels of other target PAHs. Low level PAH concentrations were annotated with a J qualifier because their concentrations were below the quantitation limit. Results of the TO-13 analyses are given in Annex E-19.

#### b. Inorganic Methods.

(1) Field Screening for Hexavalent Chromium. Seventy-six soil samples were tested in the field for water soluble hexavalent chromium with a Hach test kit. None of the 76 samples were found to contain hexavalent chromium (Annex E-20) above the quantitation limit. The limit of detection for this method is 100 parts per billion (ppb) of hexavalent chromium in soil.

(2) Soil Samples for Metal Analyses. Fifty-four soil samples were analyzed for 14 metals. Levels of calcium, magnesium, iron and aluminum generally exceeded 1,000 milligrams per kilogram (mg/kg). Chromium, lead, nickel and vanadium levels ranged between 10-80 mg/kg. Arsenic and beryllium levels ranged from less than 1 mg/kg to

4 mg/kg. The majority of the soil samples contained less than 1 mg/kg of cadmium. No mercury was detected in any of the soil samples. Results of the soil analyses for metal content are shown in Annex E-21.

(3) High Volume Filters for Metal Analyses. Twenty-four filter samples were analyzed for 14 selected metals. In **general**, the only metals detected were sodium, magnesium and calcium. Annex E-22 shows the results of these analyses.

(4) Soil Samples for Hexavalent Chromium Content. The hexavalent chromium content of 17 soil samples, stabilized in the field by passing a water extract of the soil sample through a C-18 SPE cartridge, is shown in Annex E-23. These samples were sent to the RJ Lee Group Inc. laboratory for determination of the total chromium content of the stabilized samples. No chromium was detected in the stabilized samples, thus indicating that no water soluble hexavalent chromium salts were present in the soil samples. The reported detection limit for this procedure was 3 ppb in soil. This confirms what was found by field screening with the Hach test kit.

4. QUALITY ASSURANCE. Every effort has been made to ensure that the data produced from this set of samples is of the highest quality throughout the laboratory portion of this health risk assessment. All sample analyses, with the exception of the tests for hexavalent chromium, were performed using EPA Methods. All samples were maintained under chain of custody from the time of sampling until analyses were completed. Samples were shipped to USAEHA in coolers containing dry ice, and those samples requiring refrigeration were kept at 4 °C until analysis. In many cases, matrix spike samples were prepared by the analysts and also tested along with the health risk samples. -In addition, duplicate samples were extracted and analyzed to help assess the precision of the various analytical procedures performed. Specific quality assurance procedures for the individual methodologies are discussed below.

a. EPA Ambient Air Methods for Organic Compounds.

(1) EPA Method TO-1.

(a) Extensive measures were taken to ensure that the data from the TO-1 analyses would be of the highest quality. These efforts began with exhaustive efforts to produce TO-1 cartridges free of contamination. The Tenax resin used to prepare the cartridges was solvent rinsed and thermally treated to remove VOCs which potentially could cause interferences. After the cartridges were prepared, they were thermally conditioned by heating under an inert gas purge. The cartridges were cooled to room temperature under the inert gas and sealed with gas-tight stainless steel fittings. They were kept cool until sampling was begun. Sampling must be performed no longer than 14 days after preparation of the cartridges, and

analysis be must be performed no longer than 14 days after collection. Benzene-d6 and ethylbenzene-d10 were spiked on all primary TO-1 cartridges prior to sampling to demonstrate the retentive properties of the sorbent. The sampling train was equipped with a primary cartridge followed by a backup cartridge. The purpose of the backup cartridge was to detect migration of analytes through and out the primary cartridge. After sample collection, the cartridges were resealed and shipped back to USAEHA for analysis (under cooling with dry ice). The ability to successfully recover the benzene-d6 and ethylbenzene-d10 validates the performance of the method. In addition, toluene-d8 was spiked on all cartridges immediately prior to analysis to correct for any changes in instrument response. Check standards were used to monitor the continued validity of the calibration curve. Laboratory blanks were used to assure that the thermal desorption/gas chromatographic/mass spectrometry (TD/GC/MS) system was free of contamination.

(b) Surrogate recoveries and matrix spike recoveries results are detailed in Annex E-24. In general, excellent surrogate recoveries were achieved for the benzene-d6 and ethylbenzene-d10. With the exception of R3735 and R3758, all benzene-d6 surrogate recoveries were within the quality control limits of 75-125 percent recovery. The recovery for the ethylbenzene-d10 surrogate was within the control limits for all samples. Six of the fifteen backup cartridges analyzed showed low levels of benzene-d6 ranging from 2 to 16 percent of the amount originally spiked onto the primary cartridge. This indicates some low level movement of the benzene-d6 from the primary cartridge to the backup cartridge. This was not a serious problem as the surrogate recoveries for the benzene-d6 were consistently good. None of the backup cartridges showed any traces of the ethylbenzene-d10. This indicates that ethylbenzene-d10 does not migrate through the TO-1 cartridge at the volumes collected. Seven matrix spike samples were analyzed. They were spiked with six VOCs; benzene, toluene, ethylbenzene, m/p xylene, and normal propylbenzene. Excellent recoveries were achieved for all six matrix spiked compounds. The recoveries ranged from 77 to 116 percent recovery.

(2) EPA Method TO-9. Polyurethane filters canisters were ordered from Battelle I&oratories Inc. They were certified to be free of contamination by Battelle following an extensive cleanup procedure which included compression rinsing with toluene, acetone and 5 percent ether/hexane solution. This was followed by Soxhlet extraction with a 5 percent ether/hexane solution. The canisters were sent to the EPA Stennis Space Center Laboratory for spiking with a dioxin isomer (Carbon 13 labeled 1,2,3,4-tetrachlorodibenzo-pdioxin). The spiked canisters were returned to USAEHA and used for collecting ambient air samples in Saudi Arabia and Kuwait.

(3) EPA Method TO-13. The XAD resin cartridges were ordered from Battelle. They were certified to be free of contamination by Battelle Laboratory following extensive cleanup procedures which included extracting with dichloromethane and drying under

nitrogen. The cartridges were spiked with five deuterated PAHs immediately prior to sample collection. These surrogate compounds form the basis for the determination of the efficiency of the entire method. They reflect a combination of the collection efficiency and the retentive properties of the resin, the extraction efficiency, and the stability of typical PNAs on the resin. In general, the recoveries of the surrogate compounds were within the quality control limits as set by the method. Prior to analysis, the mass spectrometer must pass stringent tuning requirements to ensure that the instrument is operating at peak performance. Annex E-25 details the tuning and surrogate recoveries results.

**b. Inorganic Methods.**

(1) Metals on High Volume Filters. A variety of quality assurance/quality control procedures are routinely employed in the analysis of the high volume filters for metal content. Such procedures include Post extract matrix spikes, duplicate samples and certified quality control check standards. In general, excellent results were obtained for the analysis of duplicate samples. Excellent recoveries were achieved for matrix spike samples. See Annex E-26 for the quality control samples results.

(2) Metals in Soil. Quality assurance/quality control procedures employed for the analysis of metals in soil are similar to those used in the analysis of metals on high volume filters. In general, excellent results were obtained for the analysis of duplicate samples as well as matrix spikes. The results of the post extraction matrix spikes, duplicate analyses and the certified quality control check standards are shown in Annex E-27.

(3) Field Screening for Hexavalent Chromium. Twenty-five soil samples were spiked with either 250, 500, or 750 ppb of hexavalent chromium. In general, good recoveries were achieved for these matrix spikes. Annex E-28 details the results of these spikes.

(4) Soil Samples Analyzed by the RJ Lee Group. Six soil matrix spike samples were analyzed by the RJ Lee Group Laboratory. Recoveries of hexavalent chromium in soil samples spiked in the field ranged from 83 to 157 percent. The results of the spike recoveries are detailed in Annex E-29.

**c. Problem Areas.** Many of the areas of concern from the Interim Kuwait health risk assessment were rectified in this assessment. A great deal of this is to be credited to experience gained from the interim assessment and to the short duration and limited scope of this assessment. However, as with any assessment, especially one in a foreign country, situations arise which can cause delays and shortcomings in the execution of the sampling plan.

(1) Due to diplomatic problems in dealing with the Saudi government, the initial sampling in Saudi Arabia had to be delayed. This caused the remainder of the sampling to be condensed into a shorter period of time.

(2) Due to the distances involved and the connections required to bring the samples back, it was difficult to get the samples to USAEHA within the holding times. All samples were able to be extracted within the holding times, however, many of the samples had to be extracted in 3 to 4 days to meet the holding times. Problems arose with the first set of samples which were to be hand-carried back by one of the departing sampling team members. The samples could not be brought back on a commercial passenger flight because of the dry ice.

(3) The high volume samplers used with the TO-13 XAD cartridges were unable to maintain sufficient air flow to deliver 325 cubic meters of air during the 24-hour sampling period. In fact, only approximately 125 cubic meters of air were sampled for the TO-13 tubes. This effectively raises the detection limit for these samples by a factor of 2.5. Although the PUF filters were able to maintain a higher flow rate, the XAD resin cartridges were chosen over the PUF filters because the XAD resin cartridges exhibited better collection efficiency for volatile PAHs and a higher retention efficiency for both volatile and reactive PAHs.



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ANNEX E-1

REFERENCES

1. Method TO-1 Method for the Determination of Volatile Organic Compounds in Ambient Air Using Tenax Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS) Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. USEPA, Revision 1.0, 1987.
2. Method TO-9 Method for the Determination of Polychlorinated Dibenzo-p-Dioxins (PCDDs) in Ambient Air Using High Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS) Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. USEPA. Revision 1.1, June 1988.
3. Method TO-13 Determination of Benzo(a)pyrene {B(a)P} and Other Polynuclear Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatographic (GC) and High Performance Liquid Chromatographic (HPLC) Analysis. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. USEPA, Revision 1.0, 1987.
4. Method 206.2 Method for the Determination of Arsenic (Atomic Absorption, Furnace Technique) Methods for Chemical Analysis of Water and Wastes. USEPA-600/4-79-020, March 1983.
5. Method 213.2 Method for the Determination of Cadmium (Atomic Absorption, Furnace Technique) Methods for Chemical Analysis of Water and Wastes. March 1983.
6. Method 239.2 Method for the Determination of Lead (Atomic Absorption Furnace Technique) Methods for Chemical Analysis of Water and Wastes. USEPA-600/4-79-020, March 1983.
7. Method 245.1 Method for the Determination of Mercury (Manual Cold Vapor Technique) Methods for Chemical Analysis of Water and Wastes. USEPA-600/4-79-020, March 1983.
8. Method 200.7 Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry Methods for the Determination of Metals in Environmental Samples, USEPA/600/4-91-010.
9. Method 6010 Inductively Coupled Plasma Atomic Emission Spectroscopy Test Methods for Evaluating Solid Waste, SW-846, revised third edition, January 1990.

10. Method 7060 Method for the Determination of Arsenic (Atomic Absorption Furnace Technique) Test Method for Evaluating Solid Wastes, SW-846, revised third edition, January 1990.

11. Method 7131 Method for the Determination of Cadmium (Atomic Absorption Furnace Technique) Test Method for Evaluating Solid Wastes, SW-846, revised third edition, January 1990.

12. Method 245.5 Method for the Determination of Mercury in Sediment (Manual Cold Vapor Technique) Methods for Chemical Analysis of Water and Wastes, USEPA/4-79-020, March 1983.

13. United States Army Environmental Hygiene Agency, Organic Environmental Chemistry Division Standard Operating Procedure (SOP) 147.1, Determination of Hexavalent Chromium in Soil, October 1993.

14. Procedure developed by **RJ Lee** for the determination of Hexavalent Chromium, November 1993.

**Final Rpt, Kuwait Oil Fire HRA No. 39-26-L192-91, 5 May - 3 Dec 91**

**ANNEX E-2**

**E-2-1**

**TITLE: Method For The Determination Of Volatile Organic Compounds In Ambient Air Using Tenax<sup>®</sup> Adsorption And Gas Chromatography/Mass Spectrometry (GC/MS)**

<b>ANALYTE:</b>	<b>CAS #</b>
Benzene	71-43-2
Toluene	108-88-3
<b>Ethyl benzene</b>	<b>100-41-4</b>
Xylenes	1330-20-7
Cumene	98-82-8
<b>n-Heptane</b>	<b>142-82-5</b>
1-Heptene	592-76-7
Chloroform	67-66-3
Carbon tetrachloride	56-23-5
1,2-Dichloroethane	107-06-2
1,1,1-Trichloroethane	71-55-6
Tetrachloroethylene	127-18-4
Trichloroethylene	79-01-6
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9
Chlorobenzene	108-90-7
Bromoform	75-25-2
Ethylene dibromide	106-93-4
<b>Bromobenzene</b>	<b>108-86-1</b>

**INSTRUMENTATION: GC/MS**

**1.0 scope**

- 1.1 The document describes a generalized protocol for collection and determination of certain **volatile** organic compounds which **can** be captured on **Tenax GC** [poly(2,6-Diphenyl phenylene oxide)] and determined by thermal desorption GC/MS techniques. Specific approaches using these techniques are described in the literature (1-3).
- 1.2 This protocol is designed to allow some flexibility in order to accommodate procedures currently **in** use. However, such flexibility also results in placement of considerable responsibility with the user to document that such procedures give acceptable **results** (i.e., documentation of **method** performance within each laboratory situation is required). Types of documentation required are described elsewhere **in** this method.

1.3 Compounds which can be determined by this method are nonpolar organics having boiling points in the range of approximately 80-200 °C. However, not all compounds falling into this category can be determined. Table 1 gives a listing of compounds for which the method has been used. Other compounds may yield satisfactory results but validation by the individual user is required.

## 2.0 Applicable Documents

2.1 ASTM standards:

D1356 Definitions of Terms Related to Atmospheric Sampling and Analysis.

E355 Recommended Practice for Gas Chromatography Terms and Relationships.

2.2 Other documents:

Existing procedures (1-3).

U.S. EPA Technical Assistance Document (4).

## 3.0 summary of Protocol

3.1 Ambient air is drawn through a cartridge containing 1-2 grams of Tenax and certain volatile organic compounds are trapped on the resin while highly volatile organic compounds and most inorganic atmospheric constituents pass through the cartridge. The cartridge is then transferred to the laboratory and analyzed.

3.2 For analysis the cartridge is placed in a heated chamber and purged with an inert gas. The inert gas transfers the volatile organic compounds from the cartridge onto a cold trap and subsequently onto the front of the GC column which is held at low temperature (e.g., -70 °C). The GC column temperature is then increased (temperature programmed) and the components eluting from the column are identified and quantified by mass spectrometry. Component identification is normally accomplished, using a library search routine, on the basis of the GC retention time and mass spectral characteristics. Less sophisticated detectors (e.g., electron capture or flame ionization) may be used for certain applications but their suitability for a given application must be verified by the user.

3.3 Due to the complexity of ambient air samples only high resolution (i.e., capillary) GC techniques are considered to be acceptable in this protocol.

#### 4.0 Significance

- 4.1 Volatile organic compounds are emitted into the atmosphere from a variety of sources including industrial and commercial facilities, hazardous waste storage facilities, etc., Many of these compounds are toxic; hence knowledge of the levels of such materials in the ambient atmosphere is required in order to determine human health impacts.
- 4.2 Conventional air monitoring methods (e.g., for work space monitoring) have relied on carbon adsorption approaches with subsequent solvent desorption. Such techniques allow subsequent injection of only a small portion, typically 1-5 of the sample onto the GC system. However, typical ambient air concentrations of these compounds require a more sensitive approach. The thermal desorption process, wherein the entire sample is introduced into the analytical (GC/MS) system fulfills this need for enhanced sensitivity.
- 5.0 Definitions used in this document and any user prepared SOPs should be consistent with ASTM D1356(6). AU abbreviations and symbols are defined with this document at the point of use.

#### 6.0 INTERFERENCES

- 6.1 Only compounds having a similar mass spectrum and GC retention time compared to the compound of interest will interfere in the method. The most commonly encountered interferences are structural isomers.
- 6.2 Contamination of the Tenax cartridge with the compound(s) of interest is a commonly encountered problem in the method. The user must be extremely careful in the preparation, storage, and handling of the cartridges throughout the entire sampling and analysis process to minimize this problem.

#### 7.0 Apparatu

- 7.1 Gas Chromatograph/Mass Spectrometry system - should be capable of subambient . temperature programming. Unit mass resolution or better up to 800 amu. Capable of scanning 30-440 amu region every 0.5-1 second. Equipped with data system for instrument control as well as data acquisition, processing and storage.
- 7.2 Thermal Desorption Unit - Designed to accommodate Tenax cartridges in use. See Figures 2a or b.
- 7.3 Sampling System - Capable of accurately and precisely drawing an air flow of LO-500 mL/minute through the Tenax cartridge. (See Figures 3a or b.)
- 7.4 Vacuum oven - connected to water aspirator vacuum supply.
- 7.5 Stopwatch.

- 7.6 Pyrex disks - for drying Tenax.
- 7.7 Glass jar - Capped with Teflon-lined screw cap. For storage of purified Tenax.
- 7.8 Powder funnel - for delivery of Tenax into cartridges.
- 7.9 Culture tubes - to hold individual glass Tenax cartridges.
- 7.10 Friction top can (paint can) - to hold clean Tenax cartridges.
- 7.11 Filter holder - stainless steel or aluminum (to accommodate 1 inch diameter filter).  
Other sizes may be used if desired. (optional)
- 7.12 Thermometer - to record ambient temperature.
- 7.13 Barometer (optional).
- 7.14 Dilution bottle - Two-liter with septum cap for standards preparation.
- 7.15 Teflon stirbar - 1 inch long.
- 7.16 Gas-tight glass syringes with stainless steel needles 10-500  $\mu\text{L}$  for standard injection onto GUMS system.
- 7.17 Liquid microliter syringes - 5.50  $\mu\text{L}$  for injecting neat liquid standards into dilution bottle.
- 7.18 Oven - 60 +/- 5-C for equilibrating dilution flasks.
- 7.19 Magnetic stirrer.
- 7.20 Heating mantel.
- 7.21 Variac.
- 7.22 Soxhlet extraction apparatus and glass thimbles - for purifying Tenax.
- 7.23 Infrared lamp - for drying Tenax.
- 7.24 GC column - SE-30 or alternative coating, glass capillary or fused Silica.
- 7.25 Psychrometer - to determine ambient relative humidity (optional).

## 8.0 Reagents and Materials

- 8.1 Empty Tenax cartridges- glass or stainless steel (See Figures 1a or b).
- 8.2 Tenax 60/80 mesh (2,6-diphenylphenylene oxide polymer).
- 8.3 Glasswool - silanized.
- 8.4 Acetone - Pesticide quality or equivalent.
- 8.5 Methanol - Pesticide quality, or equivalent.
- 8.6 Pentane - Pesticide quality or equivalent.
- 8.7 Helium- Ultra pure, compressed gas. (99.9999%)
- 8.8 Nitrogen - Ultra pure, compressed gas. (99.9999%)
- 8.9 Liquid nitrogen.
- 8.10 Polyester gloves - for handling glass Tenax cartridges.
- 8.11 Glass Fiber Filter - 1-inch diameter to fit in filter holder. (optional).
- 8.12 Perfluorotributylamine (FC- 43).
- 8.13 Chemical Standards - Neat compounds of interest. High&t purity available.
- 8.14 Granular activated charcoal - for preventing contamination of Tenax cartridges during storage . '

## 9.0 Cartridge Construction and Preparation

### 9.1 Cartridge Design

- 9.1.1 Several cartridge designs have been reported in the literature (1-3). The most common (1) is shown in Figure 1a. This design minimizes contact of the sample with metal surfaces, which can lead to decomposition in certain cases. However, a disadvantage of this design is the need to rigorously avoid contamination of the outside portion of the cartridge since the entire surface is subjected to the purge gas stream during the desorption process. Clean polyester gloves must be worn at all times when handling such cartridges and exposure of the open cartridge to ambient air must be minimized.
- 9.1.2 A second common type of design (3) is shown in Figure 1b. While this design uses a metal (stainless steel) construction, it eliminates the need to avoid direct contact with the exterior surface since only the interior of the cartridge is purged.
- 9.1.3 The thermal desorption module and sampling system must be selected to be compatible with the particular cartridge design chosen. Typical module designs are shown in Figures 2a and b. These designs are suitable for the cartridge designs shown in Figures 1a and 1b, respectively.

### 9.2 Tenax Purification

- 9.2.1 Prior to use the Tenax resin is subjected to a series of solvent extraction and thermal treatment steps. The operation should be conducted in an area where levels of volatile organic compounds (other than the extraction solvents used) are minimized.
- 9.2.2 All glassware used in Tenax purification as well as cartridge materials should be thoroughly cleaned by water rinsing followed by an acetone rinse and dried in an oven at 250 °C.
- 9.2.3 Bulk Tenax is placed in a glass extraction thimble and held in place with a plug of clean glasswool. The resin is then placed in the Soxhlet extraction apparatus and extracted sequentially with methanol and then pentane for 16-24 hours (each solvent) at approximately 6 cycles/hour. Glasswool for cartridge preparation should be cleaned in the same manner as Tenax.
- 9.2.4 The extracted Tenax is immediately placed in an open glass dish, heated under an infrared lamp for 2 hours in a hood. Care must be exercised to avoid overheating of the Tenax by the infrared lamp. The Tenax is then placed in a vacuum oven (evacuated using a water aspirator) without heating for 1 hour. An inert gas (helium or nitrogen) purge of 2-3 mL/minute is used to aid in the removal of solvent vapors. The oven temperature is then increased to 110 °C, maintaining inert gas flow and held for 1 hour. The oven temperature control is then shut off and the oven is allowed to cool to room temperature. Prior to opening the oven, the oven is slightly pressurized with

nitrogen to prevent contamination with ambient air. The Tenax is removed from the oven and sieved through a 40/60 mesh sieve (acetone rinsed and oven dried) into a clean glass vessel. If the Tenax is not to be used immediately for cartridge preparation it should be stored in a clean glass jar having a Teflon-lined screw cap and placed in a desiccator.

### 9.3 Cartridge Preparation and Pretreatment

- 9.3.1 All cartridge materials are **pre-cleaned** as described in Section 9.2.2. If the glass cartridge design shown in Figure 1a is employed all handling should be conducted wearing polyester gloves.
- 9.3.2 The cartridge is packed by placing a 0.5-1 cm glass wool plug in the base of the cartridge and then filling the cartridge to within approximately 1 cm of the top. A 0.5 cm glass wool plug is placed in the top of the cartridge.
- 9.3.3 The cartridges are then thermally conditioned by heating for 4 hours at 270 °C under an inert gas (helium) purge (100-200 mL/min).
- 9.3.4 After the 4-hour heating period the cartridges are allowed to cool. Cartridges of the type shown in Figure 1a are immediately placed (without cooling) in clean culture tubes having Teflon-lined screw caps with a glass wool cushion at both the top and the bottom. Each tube should be shaken to ensure that the cartridge is held firmly in place. Cartridges of the type shown in Figure 1b are allowed to cool to room temperature under inert gas purge and are then closed with stainless steel plugs.
- 9.3.5 The cartridges are labeled and placed in a tightly sealed metal can (e.g., paint can or similar friction top container). For cartridges of the type shown in Figure 1a the culture tube, not the cartridge, is labeled.
- 9.3.6 Cartridges should be used for sampling within 2 weeks after preparation and analyzed within 2 weeks after sampling. If possible the cartridges should be stored at -20 °C in a clean freezer (i.e., no solvent extracts or other sources of volatile organics contained in the freezer).

## 10.0 sampling

### 10.1 Flow rate and Total Volume Selection

- 10.1.1 Each compound has a characteristic retention volume (liters of air per gram of adsorbent) which must not be exceeded. Since the retention volume is a function of temperature, and possibly other sampling variables, one must include an adequate margin of safety to ensure good collection efficiency. Some considerations and guidance in this regard are provided in a recent report (5). Approximate breakthrough volumes at 38 °C (100 °F) in liters/gram of Tenax are provided in Table 1. These retention volume data

are supplied only as rough guidance and are subject to considerable variability, depending on cartridge design as well as sampling parameters and atmospheric conditions.

10.1.2 To calculate the maximum total volume of air which can be sampled use the following equation:

$$V(\text{MAX}) = \frac{V(\text{b}) * W}{1.5}$$

where:

V(MAX) = the calculated maximum total volume in liters.

V(b) = the **breakthrough** volume for the least retained compound of interest (Table 1) in liters per gram of **Tenax**.

w = the weight of **Tenax** in the cartridge, in grams.

1.5 = a dimensionless **safety** factor to allow for variability in atmospheric conditions, This factor is appropriate for temperatures in the range of 25-30 °C. If higher temperatures are encountered the factor should be **increased** (i.e., maximum total volume decreased).

10.1.3 To calculate maximum flow rate use the following equation:

$$Q_{\text{MAX}} = \frac{V(\text{MAX})}{t} * 1000$$

where:

Q(MAX) = the calculated maximum flow rate in **milliliters** per minute.

t = the desired sampling time in minutes. Times greater than 24 hours (1440 minutes) generally are unsuitable because the flow rate **required** is too low to be accurately maintained.

10.1.4 The maximum flow rate QMAX should yield a linear flow velocity of 50-500 cm/minute. Calculate the linear velocity **corresponding** to the maximum flow rate using the following equation:

$$B = \frac{Q(\text{MAX})}{\text{Pi} * r^2}$$

where:

**B** = the calculated linear flow velocity in centimeters per minute.

**r** = the internal radius of the cartridge in centimeters.

**Pi** = 3.14

If **B** is greater than 500 centimeters per minute either the total sample volume **V(MAX)** should be reduced or the sample flow rate **Q(MAX)** should be reduced by increasing the collection time. If **B** is less than 50 centimeters per minute the sampling rate **Q(MAX)** should be increased by reducing the sampling time, The total sample value **V(MAX)** cannot be increased due to component breakthrough.

- 10.1.4 The flow rate calculated as described above defines the maximum flow rate allowed. In general, one should collect additional samples in parallel, for the same time period but at lower flow rates. This practice yields a measure of quality control and is further discussed in the literature (5). In general, flow rates 2 to 4 fold lower than the maximum flow rate should be employed for the parallel samples. In all cases a constant flow rate should be achieved for each cartridge since accurate integration of the analyte concentration requires that the flow be constant over the sampling period.

## 10.2 Sample Collection

- 10.2.1 Collection of an accurately known volume of air is critical to the accuracy of the results. For this reason the use of mass flow controllers, rather than conventional needle valves or orifices is highly recommended, especially at low flow velocities (e.g., less than 100 milliliters/minute). Figure 3a illustrates a sampling system utilizing mass flow controllers. This system readily allows for collection of parallel samples. Figure 3b shows a commercially available system based on needle valve flow controllers.
- 10.2.2 Prior to sample collection insure that the sampling flow rate has been calibrated over a range including the rate to be used for sampling, with a "dummy" Tenax cartridge in place. Generally calibration is accomplished using a soap bubble flow meter or calibrated wet test meter. The flow calibration device is connected to the flow exit, assuming the entire flow system is sealed. ASTM Method D3686 describes an appropriate calibration scheme, not requiring a sealed flow system downstream of the pump.
- 10.2.3 The flow rate should be checked before and after each sample collection. If the sampling interval exceeds 4 hours the flow rate should be checked at an intermediate point during sampling as well. In general, a rotameter should be included, as showed in Figure 3b, to allow observation of the sampling flow rate without disrupting the sampling process.

- 10.2.4 To collect an air sample the cartridges are removed from the sealed container just prior to initiation of the collection process. If glass cartridges (Figure 1a) are employed they must be handled only with polyester gloves and should not contact any other surfaces.
- 10.2.5 A particulate filter and holder are placed on the inlet to the cartridges and the exit end of the cartridge is connected to the sampling apparatus. In many sampling situations the use of a filter is not necessary if only the total concentration of a component is desired. Glass cartridges of the type shown in Figure 1a are connected using teflon ferrules and Swagelok (stainless steel or teflon) fittings. Start the pump and record the following parameters on an appropriate data sheet (Figure 4): data, sampling location, time, ambient temperature, barometric pressure, relative humidity, dry gas meter reading (if applicable) flow rate, rotameter reading (if applicable), cartridge number and dry gas meter serial number.
- 10.2.6 Allow the sampler to operate for the desired time, periodically recording the variables listed above. Check flow rate at the midpoint of the sampling interval if longer than 4 hours. At the end of the sampling period record the parameters listed in 10.2.5 and check the flow rate and record the value. If the flows at the beginning and end of the sampling period differ by more than 10 the cartridge should be marked as suspect.
- 10.2.7 Remove the cartridges (one at a time) and place in the original container (use gloves for glass cartridges). Seal the cartridges or culture tubes in the friction-top can containing a layer of charcoal and package for immediate shipment to the laboratory for analysis. Store cartridges at reduced temperature (e.g., -20 °C) before analysis if possible to maximize storage stability.
- 10.2.8 Calculate and record the average sample rate for each cartridge according to the following equation:

$$Q(A) = \frac{Q_1 + Q_2 + \dots + Q_N}{N}$$

where:

$Q(A) =$  Average flow rate in mL/minute.

$Q_1 + Q_2 \dots + Q_N =$  Flow rates determined at beginning, end, and intermediate points during sampling.

$N =$  Number of points averaged.

10.2.9 Calculate and record the total volumetric flow for each cartridge using the following equation:

$$V(m) = \frac{T * Q(A)}{1000}$$

where:

V(m) = Total volume sampled in liters at measured temperature and pressure.

T2 = stop time.

T1 = start time.

T = sampling time = T2 - T1, minutes

10.2.10 The total volume V(s) at standard conditions. 25 °C and 760 mm Hg, is calculated from the following equation:

$$V(s) = V(m) * \frac{P(A)}{760} * \frac{273}{273 + t(a)}$$

where:

P(A) = Average barometric pressure, mm Hg

t(A) = Average ambient temperature, -C.

## 11 .O GC/MS Analysis

### 11.1 Instrument Set-Up

- 11.1.1 Considerable variation from one laboratory to another is expected in terms of instrument configuration. Therefore each laboratory must be responsible for verifying that their particular system yields satisfactory results. Section 14 discusses specific performance criteria which should be met.
- 11.1.2 A block diagram of the typical GC/MS system required for analysis of Tenax cartridges is depicted in Figure 5. The operation of such devices is described in 11.2.4. The thermal desorption module must be designed to accommodate the particular cartridge configuration. Exposure of the sample to metal surfaces should be minimized and only stainless steel, or nickel metal surfaces should be employed. The volume of tubing and fittings leading from the cartridge to the GC column must be minimized and all areas must be well-swept by helium carrier gas.

- 11.1.3 The GC column inlet should be capable of being cooled to  $-70\text{ }^{\circ}\text{C}$  and subsequently increased rapidly to approximately  $30\text{ }^{\circ}\text{C}$ . This can be most readily accomplished using a GC equipped with subambient cooling capability (liquid nitrogen) although other approaches such as manually cooling the inlet of the column in liquid nitrogen may be acceptable.
- 11.1.4 The specific GC column and temperature program employed will be dependent on the specific compounds of interest. Appropriate conditions are described in the literature (1-3). In general a nonpolar stationary phase (e.g., SE-30, OV-1) temperature programmed from  $30\text{-C}$  to  $200\text{-C}$  at 8 degrees/minute will be suitable. Fused silica bonded phase columns are preferable to glass columns since they are more rugged and can be inserted directly into the MS ion source, thereby eliminating the need for a GUMS transfer line.
- 11.1.5 Capillary column dimensions of 0.3 mm ID and 50 meters long are generally appropriate although shorter lengths may be sufficient in many cases.
- 11.1.6 Prior to instrument calibration or sample analysis the GUMS system is assembled as shown in Figure 5. Helium purge flows (through the cartridge) and carrier flow are set at approximately 10 mL/minute and 1-2 mL/minute, respectively. If applicable the injector sweep flow is set at 2-4 mL/minute.
- 11.1.7 Once the column and other system components are assembled and the various flows established the column temperature is increased to  $250\text{-C}$  for approximately 4 hours (or overnight if desired) to condition the column.
- 11.1.8 The MS and data system are set according to the manufacturer's instructions. Electron impact ionization (70eV) and an electron multiplier gain of approximately  $5 \times 10^4$  should be employed. Once the entire GC/MS system has been setup the system is calibrated as described in Section 11.2. The user should prepare a detailed standing operating procedure (SOP) describing this process for the particular instrument being used.

## 11.2 Instrument Calibration

- 11.2.1 Tuning and mass standardization of the MS system is performed according to manufacturer's instructions and relevant information from the user prepared SOP. Perfluorotributylamine should generally be employed for this purpose. The material is introduced directly into the ion source through a molecular leak. The instrumental parameters (e.g., lens voltages, resolution, etc.) should be adjusted to give the relative ion abundances shown in Table 2 as well as acceptable resolution and peak shape. If these approximate relative abundances cannot be achieved, the ion source may require cleaning according to manufacturer's instructions. In the event that the user's instrument cannot achieve these relative ion abundances, but is otherwise operating properly, the user may adopt another set of relative abundances as performance criteria. However, these alternate values must be repeatable on a &y-to-day basis.

- 11.2.2 After the mass standardization and tuning process has been completed and the appropriate values entered into the data system the user should then calibrate the entire system by introducing known quantities of the standard components of interest into the system. **Three** alternate procedures may be employed for the calibration process including 1) direct syringe injection of dilute vapor phase standards, prepared in a dilution bottle, onto the GC column, 2) Injection of dilute vapor phase standards into a carrier gas stream directed through the **Tenax** cartridge, and 3) **introduction** of permeation or diffusion tube standards onto a **Tenax** cartridge. The standards preparation procedures for each of these approaches are **described** in Section 13. The following paragraphs describe the instrument calibration **process** for each of these approaches.
- 11.2.3 If the instrument is to be calibrated by direct injection of a gaseous standard, a standard is prepared in a dilution bottle as described in Section 13.1. The GC column is cooled to **-70-C** (or, alternately a portion of the column inlet is manually cooled with liquid nitrogen). The MS and data system is set up for acquisition as described in the relevant user SOP. The ionization filament should be turned off during the initial 2-3 minutes of the run to allow oxygen and other highly volatile components to **elute**. An appropriate volume (less than 1 mL) of the gaseous standard is injected onto the GC system using an accurately calibrated gas tight syringe. The system **clock** is started and the column is maintained at **-70-C** (or liquid nitrogen inlet cooling) for 2 minutes. The column temperature is rapidly **increased** to the desired initial temperature (e.g., 30-C). The temperature program is **started** at a consistent time (e.g., 4 minutes) **after** injection. **Simultaneously** the **ionization** filament is turned on and data acquisition is initiated. After the **last** component of interest has eluted acquisition is terminated and the data is processed as described in Section 11.2.5. The **standard** injection process is repeated using different standard volumes as desired.
- 11.2.4 If the system is to be calibrated by analysis of spiked **Tenax** cartridges a set of **cartridges** is prepared as described in Sections 13-2 or 13.3. Prior to analysis the cartridges are stored as described in Section 9.3. If glass **cartridges** (Figure 1a) are employed **care** must be taken to avoid direct contact, as described earlier. The GC column is cooled to **-70-C**, the **collection** loop is immersed in liquid nitrogen and the desorption module is maintained at 250-C. The inlet valve is **placed** in the **desorb** mode and the standard cartridge is placed in the desorption module, making certain that no leakage of purge gas occurs. The **cartridge** is purged for 10 minutes and then the inlet valve is placed in the inject mode and the liquid nitrogen source **removed** from the collection trap. The GC column is maintained at **-70-C** for **two** minutes and **subsequent** steps are as described in 11.2.3. After the process is complete the **cartridge** is removed from the desorption module and stored for subsequent use as **described** in Section 9.3.

11.2.5 Data processing for instrument calibration involves determining retention times, and integrated characteristic ion intensities for each of the compounds of interest. In addition, for at least one chromatographic run, the individual mass spectra should be inspected and compared to reference spectra to ensure proper instrumental performance. Since the steps involved in data processing are highly instrument specific, the user should prepare a SOP describing the process for individual use. Overall performance criteria for instrument calibration are provided in Section 14. If these criteria are not achieved the user should refine the instrumental parameters and/or operating procedures to meet these criteria.

### 11.3 Sample Analysis

11.3.1 The sample analysis process is identical to that described in Section 11.2.4 for the analysis of standard Tenax cartridges.

11.3.2 Data processing for sample data generally involves 1) qualitatively determining the presence or absence of each component of interest on the basis of a set of characteristic ions and the retention time using a reverse-search software routine, 2) quantification of each identified component by integrating the intensity of a characteristic ion and comparing the value to that of the calibration standard, and 3) tentative identification of other components observed using a forward (library) search software routine. As for other user specific processes, a SOP should be prepared describing the specific operations for each individual laboratory.

### 12.0 Calculations

#### 12.1 Calibration Response Factors

12.1.1 Data from calibration standards is used to calculate a response factor for each component of interest. Ideally the process involves analysis of at least three calibration levels of each component during a given day and determination of the response factor (area/nanogram injected) from the linear least squares fit of a plot of nanograms injected, versus area (for the characteristic ion). In general quantities of component greater than 1,000 nanograms should not be injected because of column overloading and/or MS response nonlinearity.

12.1.2 In practice the daily routine may not always allow analysis of such calibration standards. In this situation calibration data from consecutive days may be pooled to yield a response factor, provided that analysis of replicate standards of the same concentration are shown to agree within 20% on the consecutive days. One standard concentration, near the midpoint of the analytical range of interest, should be chosen for injection every day to determine day-to-day response reproducibility.

12.1.3 If substantial nonlinearity is present in the calibration curve a nonlinear least squares fit (e.g., quadratic) should be employed. This process involves fitting the data to the following equation:

$$Y = A + BX + CX^2$$

where:

**Y** = peak area

**X** = quantity of component, nanograms

**A, B, and C** are coefficients in the equation

## 12.2 Analyte Concentrations

12.2.1 Analyte quantities on a sample cartridge are calculated from the following equation:

$$YA = A + BXA + CXA$$

where:

**YA** is the **area** of the analyte characteristic ion for the sample cartridge.

**XA** is the calculated quantity of analyte on the sample cartridge, in **nanograms**.

**A, B, and C** are the **coefficients** calculated from the calibration curve described in Section 12.1.3.

12.2.2 If instrumental response is essentially **linear** over the concentration range of interest a **linear** equation (**C=0** in the equation above) can be employed.

12.2.3 Concentration of analyte in the original air sample is calculated from the following equation:

$$CA = \frac{XA}{VS}$$

where:

**CA** = the calculated concentration of analyte in nanograms per liter.

**VS** and **XA** are as previously defined in Section 10.2.10 and 12.2.1, respectively.

## 13.0 Standard Preparation

### 13.1 Direct Injection

- 13.1.1 This process involves **preparation** of a dilution bottle containing the desired concentrations of compounds of interest for direct injection onto the GC/MS system.
- 13.1.2 Fifteen **3-millimeter** diameter glass **beads** and a 1-inch Teflon **stirbar** are placed in a clean **2-liter** glass septum **capped** bottle and the exact volume is determined by weighing the bottle before and after **filling** with deionized water. The bottle is then rinsed with acetone and dried at 200-C.
- 13.1.3 The amount of each standard to be injected into the vessel is calculated from the desired injection quantity and volume using the following equation:

$$WT = \frac{WI}{VI} * VB$$

where:

WT is the total quantity of analyte to be injected into the bottle in milligrams.

WI is the desired weight of analyte to be injected onto the GUMS system or spiked cartridge in nanograms.

VI is the **desired GC/MS or cartridge injection volume** (should not exceed 500) in microliters.

VB is total volume of dilution bottle determined in 13.1.1, in liters.

- 13.1.4 The volume of the neat standard to be injected into the dilution bottle is determined using the following equation:

$$VT = \frac{WT}{d}$$

where:

VT is the total volume of neat liquid to be injected in **microliters**.

d is the density of the neat standard in grams per milliliter.

- 13.1.5 The bottle is placed in a **60-C** oven for at **least** 30 minutes prior to removal of a **vapor** phase standard.
- 13.1.6 To withdraw a standard for GUMS injection the bottle is removed from the oven and stirred for 10-15 seconds. A suitable gas-tight **microber** syringe **warmed** to 60-C, is inserted through the septum cap and pumped three times

slowly. The appropriate volume of sample (approximately 25 % larger than the desired injection volume) is drawn into the syringe and the volume is adjusted to the exact value desired and then immediately injected over a 5-10 seconds period onto the GUMS system as described in Section 11.2.3.

### 13.2 Preparation of Spiked Cartridges by Vapor Phase Injection

13.2.1 This process involves **preparation** of a dilution **bottle** containing the desired concentrations of the compound(s) of interest as **described** in 13.1 and injecting the desired volume of **vapor** into a flowing inert gas stream directed through a clean **Tenax** cartridge. 13.2.2 A helium purge system is assembled wherein the helium flow 20-30 mL/minute is passed through a stainless steel tee fitted with a septum injector. The clean **Tenax** cartridge is connected downstream of the tee using appropriate Swagelok fittings. Once the cartridge is placed in the flowing gas **stream** the appropriate volume vapor standard, in the dilution bottle, is **injected** through the septum as described in 13.1.6. The syringe is flushed **several** times by alternately **filling** the syringe with carrier gas and displacing the contents into the flow stream, without removing the syringe from the septum. Carrier flow is maintain through the cartridge for approximately 5 minutes after injection.

### 13.3 Preparation of Spiked Traps Using Permeation or Diffusion Tubes

- 13.3.1 A flowing **stream** of inert gas containing known amounts of each Compound of interest is generated according to ASTM Method D3609(6). Note that a method of accuracy maintaining temperature within +/-0.1-C is required and the system generally must be equilibrated for at least 48 hours before use.
- 13.3.2 An accurately known volume of the standard gas stream (usually 0.1-1 liter) is drawn through a clean **Tenax** cartridge using the sampling system described in Section 10.2.1, or a similar system. However, if mass flow controllers are employed they must be calibrated for the carrier gas used in Section 13.3.1 (usually nitrogen). Use of air as the carrier gas for permeation systems is not recommended, unless the compounds of interest are known to be highly stable in air.
- 13.3.3 The spiked cartridges are then stored or immediately analyzed as in Section 11.2.4.

### 14.0 Performance Criteria and Quality Assurance

This section summaries quality assurance (QA) measures and provides guidance concerning performance criteria which should be achieved 'within each laboratory. In many cases the **specific** QA procedures have **been described** within the appropriate section describing the particular activity (e.g., parallel sampling).

## 14.1 standing Operating Procedures (SOPS)

- 14.1.1 Each user should generate SOPS describing the following activities as they are performed in their laboratory: 1) assembly, calibration, and operation of the sampling system, 2) preparation, handling and storage of Tenax cartridges, 3) assembly and operation of GUMS system including the thermal desorption apparatus and data system, and 4) all aspects of data recording and processing.
- 14.1.2 SOPS should provide specific step-wise instructions and should be readily available to, and understood by the laboratory personnel conducting the work.

## 14.2 Tenax Cartridge Preparation

- 14.2.1 Each batch of Tenax cartridges prepared (as described in Section 9) should be checked for contamination by analyzing one cartridge immediately after preparation. While analysis can be accomplished by GC/MS, many laboratories may choose to use GC/FID due to logistical and cost considerations.
- 14.2.2 Analysis by GC/FID is accomplished as described for GUMS (Section 11) except for use of FID detection.
- 14.2.3 While acceptance criteria can vary depending on the components of interest, at a minimum the clean cartridge should be demonstrated to contain less than one fourth of the minimum level of interest for each component. For most compounds the blank level should be less than 10 nanograms per cartridge in order to be acceptable. More rigid criteria may be adopted, if necessary, within a specific laboratory. If a cartridge does not meet these acceptance criteria the entire lot should be rejected.

## 14.3 Sample Collection

- 14.3.1 During each sampling event at least one clean cartridge will accompany the samples to the field and back to the laboratory, without being used for sampling, to serve as a field blank. The average amount of material found on the field blank cartridge may be subtracted from the amount found on the actual samples. However, if the blank level is greater than 25 % of the sample amount, data for that component must be identified as suspect.
- 14.3.2 During each sampling event at least one set of parallel samples (two or more samples collected simultaneously) will be collected, preferably at different flow rates as described in Section 10.1. If agreement between parallel samples is not generally within +/-25% the user should collect parallel samples on a much more frequent basis (perhaps for all sampling points). If a trend of lower apparent concentrations with increasing flow rate is observed for a set of parallel samples one should consider using a reduced flow rate

and longer sampling interval if possible. If this practice does not improve the reproducibility further evaluation of the method performance for the compound of interest may be required.

- 14.3.3 Backup cartridges (two cartridges in series) should be collected with each sampling event. Backup cartridges should contain less than 20% of the amount of components of interest found in the front cartridges, or be equivalent to the blank cartridge level, whichever is greater. The frequency of use of backup cartridges should be increased if increased flow rate is shown to yield reduced component levels for parallel sampling. This practice will help to identify problems arising from breakthrough of the component of interest during sampling.

#### 14.4 GC/MS Analysis

- 14.4.1 Performance criteria for MS tuning and mass calibration have been discussed in Section 11.2 and Table 2. Additional criteria may be used by the laboratory if desired. The following sections provide performance guidance and suggested criteria for determining the acceptability of the GUMS system.
- 14.4.2 Chromatographic efficiency should be evaluated using spiked Tenax cartridges since this practice tests the entire system. In general a reference compound such as perfluorotoluene should be spiked onto a cartridge at the 100 nanogram level as described in Section 13.2 or 13.3. The cartridge is then analyzed by GC/MS as of parallel samples one should consider using a reduced flow rate and longer sampling interval if possible. If this practice does not improve the reproducibility further evaluation of the method performance for the compound of interest may be required.
- 14.3.3 Backup cartridges (two cartridges in series) should be collected with each sampling event. Backup cartridges should contain less than 20% of the amount of components of interest found in the front cartridges, or be equivalent to the blank cartridge level, whichever is greater. The frequency of use of backup cartridges should be increased if increased flow rate is shown to yield reduced component levels for parallel sampling. This practice will help to identify problems arising from breakthrough of the component of interest during sampling.

#### 14.4 GC/MS Analysis

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- 14.4.2 Chromatographic efficiency should be evaluated using spiked Tenax cartridges since this practice tests the entire system. In general a reference compound such as perfluorotoluene should be spiked onto a cartridge at the 100

nanogram level as described in Section 13.2 or 13.3. The cartridge is then analyzed by GUMS as described in Section 11.4. The perfluorotoluene (or other reference compound) peak is then plotted on an expanded time scale so that its width at 10% of the peak can be calculated, as shown in Figure 6. The width of the peak at 10% height should not exceed 10 seconds. More stringent criteria may be required for certain applications. The asymmetry factor (see Figure 6) should be between 0.8 and 2.0. The asymmetry factor for any polar or reactive compounds should be determined using the process described above. If peaks are observed that exceed the peak width or asymmetry factor criteria above, one should inspect the entire system to determine if unswept zones or cold spots are present in any of the fittings and is necessary. Some laboratories may chose to evaluate column performance separately by direct injection of a test mixture onto the GC column. Suitable schemes for column evaluation have been reported in the literature (7). Such schemes cannot be conducted by placing the substances onto Tenax because many of the compounds (e.g., acids, bases, alcohols) contained in the test mix are not retained, or degrade, on Tenax.

- 14.4.3 The system detection limit for each component is calculated from the data obtained for calibration standards. The detection limit is defined as:

$$DL = A + 3.3S$$

where:

DL is the calculated detection limit in nanograms injected.

A is the intercept calculated in Section 12.1.1 or 12.1.3.

S is the standard deviation of replicate determinations of the lowest level standard (at least three such determinations are required).

In general the detection limit should be 20 nanograms or less and for many applications detection limits of 1-5 nanograms may be required. The lowest level standard should yield a signal to noise ratio from the total ion current response, of approximately 5.

- 14.4.4 The relative standard deviation for replicate analyses of cartridges spiked at approximately 10 times the detection limit should be 20% or less. Day to day relative standard deviation should be 25% or less.
- 14.4.5 A useful performance evaluation step is the use of an internal standard to track system performance. This is accomplished by spiking each cartridge, including blank, sample, and calibration cartridges with approximately 100 nanograms of a compound not generally present in ambient air (e.g., perfluorotoluene). The integrated ion intensity for this compound helps to identify problems with a specific sample. In general the user should calculate the standard deviation of the internal standard response for a given set of samples analyzed under identical tuning and calibration conditions. Any

sample giving a value greater than  $\pm 2$  standard deviations from the mean (calculated excluding that particular sample) should be identified as suspect. Any marked change in internal standard response may indicate a need for instrument recalibration.

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6. *Annual Book of ASTM Standards*. Part 11.03, "Atmospheric Analysis," American Society for Testing and Material, Philadelphia, Pennsylvania.
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**TABLE 1. RETENTION VOLUME ESTIMATES FOR COMPOUNDS ON TENAX**

<b>COMPOUND</b>	<b>ESTIMATED RETENTION VOLUME AT 100-F ( 38-C ) - LITERS/GRAM</b>
Benzene	19
Toluene	97
Ethyl Benzene	200
Xylene (s)	-200
Cumene	440
n-Heptane	20
1-Heptene	40
Chloroform	8
Carbon Tetrachloride	8
1,2-Dichloroethane	10
1,1 ,1-Trichloroethane	6
Tetrachloroethylene	80
Trichloroethylene	20
1,2-Dichloropropane	30
1,3-Dichloropropane	90
Chlorobenzene	150
Bromoform	100
Ethylene Dibromide	60
Bromobenzene	300

**TABLE 2. SUGGESTED PERFORMANCE CRITERIA FOR RELATIVE ION  
ABUNDANCES FROM FC-43 MASS CALIBRATION**

<b>M/E</b>	<b>% RELATIVE ABUNDANCE</b>
51	1.8 +/- 0.5
69	100
100	12.0 +/- 1.5
119	12.0 +/- 1.5
131	35.0 +/- 3.5
219	24.0 +/- 2.5
264	3.7 +/- 0.4
314	0.25 +/- 0.1

Final Rpt, Kuwait Oil Fire HRA No. 39-26-L192-91, 5 May - 3 Dec 91

ANNEX E-3

E-3-1

**TITLE: Method For The Determination Of Polychlorinated Dibenzo-p-Dioxins (PCDDs) In Ambient Air Using High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS)**

**ANALYTE:**

CAS #

**PCDD**

1,2,3,4-tetrachlorodibenzo-p-dioxin

1,2,3,4-TCDD

1,2,3,4,7,8-hexachlorodibenzo-p-dioxin

1,2,3,4,7,8-HxCDD

Octachlorodibenzo-p-dioxin

**OCDD**

2,3,7,8-Tetrachlorodibenzo-p-dioxin

2,3,7,X-TCDD

1746-01-6

**INSTRUMENTATION: GC/MS****1.0 scope**

**1.1** This document describes a method for the **determination of polychlorinated dibenzo-p-dioxins (PCDDs) in ambient air**. In particular, **the following PCDDs have been evaluated in the laboratory utilizing this method:**

- 1,2,3,4-tetrachlorodibenzo-p-dioxin (1,2,3,4-TCDD)
- 1,2,3,4,7,8-hexachlorodibenzo-p-dioxin (1,2,3,4,7,8-HxCDD)
- Octachlorodibenzo-p-dioxin (OCDD)
- 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)

The method consists of sampling ambient air via an inlet filter followed by a cartridge (filled with polyurethane foam) and analysis of the sample using high-resolution gas chromatography/ high-resolution mass spectrometry (HRGC/HRMS). Original laboratory studies have indicated that the use of polyurethane foam (PUF) or silica gel in the sampler will give equal efficiencies for retaining PCDD/PCDF isomers; i.e., the median retention efficiencies for the PCDD isomers ranged from 67 to 124 percent with PUF and from 47 to 133 percent with silica gel. Silica gel, however, produced lower levels of background interferences than PUF. The detection limits were, therefore, approximately four times lower for tetrachlorinated isomers and ten times lower for hexachlorinated isomers when using silica gel as the adsorbent. The difference in detection limit was approximately a factor of two for the octachlorinated isomers. However, due to variable recovery and extensive cleanup required with silica gel, the method has been written using PUF as the adsorbent.

- 1.2 With careful attention to reagent purity and other factors, the method can detect PCDDs in filtered air at levels below 1 - 5 pg/m3\*.

\* Lowest levels for which the method has been validated. Up to an order of magnitude better sensitivity should be achievable with 24-hour air samples.

- 1.3 Average recoveries ranged from 68 percent to 140 percent in laboratory evaluations of the method sampling ultrapure filtered air. Percentage recoveries and sensitivities obtainable for ambient air samples have not been determined.

## 2.0 Applicable Documents

### 2.1 ASTM Standards

- 2.1.1 Method D1356 - Definitions of Terms Relating to Atmospheric Sampling and Analysis.
- 2.1.2 Method E260 - Recommended Practice for General Gas Chromatography procedures.
- 2.1.3 Method E355 - Practice for Gas Chromatography Terms and Relationships.

### 2.2 EPA Documents

- 2.2.1 Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II - "Ambient Air Specific Methods," Section 2.2 - "Reference Method for the Determination of Suspended Particulates in the Atmosphere," Revision 1, July 1979! EPA-600/4-77-027A.
- 2.2.2 Protocol for the Analysis of 2,3,7,8-Tetrachlorodibenzop-Dioxin by High Resolution Gas Chromatography-High Resolution Mass Spectrometry, U.S. Environmental Protection Agency, January 1986, EPA-600/4-86-004.
- 2.2.3 Evaluation of an EPA High Volume Air Sampler for Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzo-furans, undated report by Battelle under Contract 68-024127, Project Officers Robert G. Lewis and Nancy K. Win, U.S. Environmental Protection Agency, EMSL, Research Triangle Park, North Carolina.
- 2.2.4 Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, U.S. Environmental Protection Agency, April 1984, 600/4-84-041.
- 2.2.5 Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air, U.S. Environmental Protection Agency, June 1983, EPA-600/4-83-027.

## 2.3 Other Documents

- 2.3.1 General Metal Works Operating Procedures for Model PS-1 Sampler, General Metal Works, Inc., Village of Cleves, Ohio.
- 2.3.2 Chicago Air Quality: PCB Air Monitoring Plan, Phase 2, Illinois Environmental Protection Agency, Division of Air Pollution Control, April 1986, IEPA/APC/86-011.

## 3.0 Summary of Method

- 3.1 Filters and adsorbent cartridges (containing PUF) are cleaned in solvents and vacuum-dried. The filters and adsorbent cartridges are stored in screw-capped jars wrapped in aluminum foil (or otherwise protected from light) before careful installation on a modified high volume sampler.
- 3.2 Approximately 325 m3 of ambient air is drawn through a cartridge on a calibrated General Metal Works Model PS-1 Sampler, or equivalent (breakthrough has not been shown to be a problem with sampling volumes of 325 m3).
- 3.3 The amount of air sampled through the adsorbent cartridge is recorded, and the cartridge is placed in an appropriately labeled container and shipped along with blank adsorbent cartridges to the analytical laboratory for analysis.
- 3.4 The filters and PUF adsorbent cartridge are extracted together with benzene. The extract is concentrated, diluted with hexane, and cleaned up using column chromatography.
- 3.5 The High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS) system is verified to be operating properly and is calibrated with five concentration calibration solutions, each analyzed in triplicate.
- 3.6 A preliminary analysis of a sample of the extract is performed to check the system performance and to ensure that the samples are within the calibration range of the instrument. If necessary, recalibrate the instrument, adjust the amount of the sample injected, adjust the calibration solution concentration, and adjust the data processing system to reflect observed retention times, etc.
- 3.7 The samples and the blanks are analyzed by HRGC/HRMS and the results are used (along with the amount of air sampled) to calculate the concentrations of polychlorinated dioxins in ambient air.

## 4.0 Significance

- 4.1 Polychlorinated dibenzo-p-dioxins (PCDDs) are extremely toxic. They are carcinogenic and are of major environmental concern. Certain isomers, for example, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), have LD50 values in the parts-per-trillion range for some animal species. Major sources of these compounds have been commercial processes involving polychlorinated phenols and polychlorinated biphenyls (PCBs). Recently, however, combustion sources have been shown to emit

polychlorinated dibenzo-p-dioxin (PCDD), including the open-flame combustion of wood containing chlorophenol wood preservatives, and emissions from burning transformers and/or capacitors that contain PCBs and chlorobenzenes.

- 4.2 Several documents have been published which describe sampling and analytical approaches for PCDDs, as outlined in Section 2.2. The attractive features of these methods have been combined in this procedure. This method has not been validated in its final form, and, therefore, one must use caution when employing it for specific applications.
- 4.3 The relatively low level of PCDDs in the environment requires the use of high volume sampling techniques to acquire sufficient samples for analysis. However, the volatility of PCDDs prevents efficient collection on filter media. Consequently, this method utilizes both a filter and a PUF backup cartridge which provides for efficient collection of most PCDDs.

## 5 . 0 Definitions

Definitions used in this document and in any user-prepared standard operating procedures (SOPs) should be consistent with ASTM Methods D1356 and E355 (Sections 2.1.1 and 2.1.3). All abbreviations and symbols within this document are defined the first time they are used.

## 6.0 Interferences

- 6.1 Chemicals that elute from the gas chromatographic (GC) column within +/-10 scans of the standards or compounds of interest and which produce, within the retention time windows, ions with any mass-to-charge (m/e) ratios close enough to those of the ion fragments used to detect or quantify the analyte compounds are potential interferences. Most frequently encountered potential interferences are other sample components that are extracted along with PCDDs, e.g., polychlorinated biphenyls (PCBs), methoxybiphenyls, chlorinated hydroxydiphenylethers, chlorinated naphthalenes, DDE, DDT, etc. The actual incidence of interference by these compounds also depends upon relative concentrations, mass spectrometric resolution, and chromatographic conditions. Because very low levels of PCDDs must be measured, the elimination of interferences is essential. High-purity reagents and solvents must be used and all equipment must be scrupulously cleaned. Laboratory reagent blanks must be analyzed to demonstrate absence of contamination that would interfere with the measurements. Column chromatographic procedures are used to remove some coextracted sample components; these procedures must be performed carefully to minimize loss of analyte compounds during attempts to increase their concentration relative to other sample components.
- 6.2 In addition to chemical interferences, inaccurate measurements could occur if PCDDs are retained on particulate matter, the filter, or PUF adsorbent cartridge, or are chemically changed during sampling and storage in ways that are not accurately measured by adding isotopically labeled spikes to the samples.

6.3 The system cannot separately quantify gaseous PCDDs and particulate PCDDs because the material may be lost from the filter by volatilization after collection and may be transferred to the absorbent cartridge. Gaseous PCDDs may also be adsorbed on particulate matter on the filter.

## 7.0 Apparatus

7.1 General Metal Works (GMW) Model PS-1 Sampler.

7.2 At least two Model PS-1 sample cartridges and filters per PS-1 Sampler.

7.3 Calibrated GMW Model 40 calibrator.

7.4 High-Resolution Gas Chromatograph/High-Resolution Mass Spectrometer/Data System (HRGC/HRMS/DS).

7.4.1 The GC must be equipped for temperature programming, and all required accessories must be available, including syringes, gases, and a capillary column. The GC injection port must be designed for capillary columns. The use of splitless injection techniques is recommended. On-column injection techniques can be used but they may severely reduce column lifetime for nonchemically bonded columns. In this protocol, a 2- $\mu\text{L}$  injection volume is used consistently. With some GC injection ports, however, 1- $\mu\text{L}$  injections may produce some improvement in precision and chromatographic separation. A 1- $\mu\text{L}$  injection volume may be used if adequate sensitivity and precision can be achieved.

NOTE: If 1  $\mu\text{L}$  is used as the injection volume, the injection volumes for all extracts, blanks, calibration solutions and performance check samples must be 1  $\mu\text{L}$ .

7.4.2 Gas Chromatograph-Mass Spectrometer Interface. The gas chromatograph is usually coupled directly to the mass spectrometer source. The interface may include a diverter valve for shunting the column effluent and isolating the mass spectrometer source. All components of the interface should be glass or glass-lined stainless steel. The interface components should be compatible with 300-C temperatures. Cold spots and/or active surfaces (adsorption sites) in the GUMS interface can cause peak tailing and peak broadening. It is recommended that the GC column be fitted directly into the MS source. Graphic ferrules should be avoided in the GC injection area since they may adsorb TCDD. Vespel(R) or equivalent ferrules are recommended.

7.4.3 Mass Spectrometer. The static resolution of the instrument must be maintained at a minimum of 10,000 (10 percent valley). The mass spectrometer must be operated in a selected ion monitoring (SIM) mode with a total cycle time (including voltage reset time) of one second or less (Section 12.3.4.1). At a minimum, ions that occur at the following masses must be monitored:

2,3,7,8-TCDD	1,2,3,4,7,8-HxCDD	OCDD
258.9300	326.8521	394.7742
319.8965	389.8156	457.7377
321.8936	391.8127	459.7347
331.9368		
333.93338		

- 7.4.4 **Data System.** A dedicated computer data system is employed to control the rapid multiple ion monitoring process and to acquire the data. Quantification data (peak areas or peak heights) and SIM traces (displays of intensities of each m/z being monitored as a function of time) must be acquired during the analyses. Quantifications may be reported based upon computer-generated peak areas or upon measured peak heights (chart recording). The detector zero setting must allow peak-to-peak measurement of the noise on the baseline.
- 7.4.5 **GC Column.** A fused silica column (30 m x 0.25 mm I.D.) coated with DB-5, 0.25  $\mu$  film thickness (J & S Scientific, Inc., Crystal Lake, IL) is utilized to separate each of the several tetrathrough octa-PCDDs, as a group, from all of the other groups. This column also resolves 2,3,7,8-TCDD from all 21 other TCDD isomers; therefore, 2,3,7,8-TCDD can be determined quantitatively if proper calibration procedures are followed as per Sections 12.3 through 12.6. Other columns may be used for determination of PCDDs, but separation of the wrong PCDD isomers must be demonstrated and documented. Minimum acceptance criteria must be determined as per Section 12.1. At the beginning of each 12-hour period (after mass resolution has been demonstrated) during which sample extracts or concentration calibration solutions will be analyzed, column operating conditions must be attained for the required separation on the column to be used for samples.
- 7.5 AU required syringes, gases, and other pertinent supplies to operate the HRGCIHRMS system.
- 7.6 Airtight, labeled screw-capped containers to hold the sample cartridges (preferably glass with Teflon seals or other noncontaminating seals).
- 7.7 Data sheets for each sample for recording the location and sample time, duration of sample, starting time, and volume of air sampled.
- 7.8 Balance capable of weighing accurately to  $\pm 0.001$  g.
- 7.9 Pipettes, micropipets, syringes, burets, etc., to make calibration and spiking solutions, dilute samples if necessary, etc., including syringes for accurately measuring volumes such as 25  $\mu$ L and 100  $\mu$ L of isotopically labeled dioxin solutions.
- 7.10 Soxhlet extractors capable of extracting GMW PS-1 PUF adsorbent cartridges (2.3" x 5" length), 500-mL flask, and condenser.
- 7.11 Vacuum drying oven system capable of maintaining the PUF cartridges being evacuated at 240 torr (flushed with nitrogen) overnight.

- 7.12 Ice chest - to store samples at O-C after collection.
- 7.13 Glove box for working with extremely toxic standards and reagents with explosion-proof hood for venting fumes from solvents reagents, etc.
- 7.14 Adsorbion columns for column chromatography - 1 cm x 10 cm and 1 cm x 30 cm, with stands.
- 7.15 Concentrator tubes and a nitrogen evaporation apparatus with variable flow rate.
- 7.16 Laboratory refrigerator with chambers operating at O-C and 4-C.
- 7.17 Kuderna-Danish apparatus - 500 mL evaporating flask, 10 mL graduated concentrator tubes with ground-glass stoppers, and 3-ball macro Snyder Column (Kontes K-570001-0500, K-50300-0121, and K-569001-219, or equivalent).
- 7.18 Two-ball micro Snyder Column, Kuderna-Danish (Kontes 569001-0219, or equivalent).
- 7.19 Stainless steel spatulas and spoons.
- 7.20 Minivials - 1 mL, borosilicate glass, with conical reservoir and screw caps lined with Teflon-faced silicone disks, and a vial holder.
- 7.21 Chromatographic columns for Carbopak cleanup - disposable 5-mL graduated glass pipets, 6 to 7 mm ID.
- 7.22 Desiccator.
- 7.23 Polyester gloves for handling PUF cartridges and filter.
- 7.24 Die - to cut PUF plugs.
- 7.25 Water bath equipped with concentric ring cover and capable of being temperature-controlled within +/-2-C.
- 7.26 Erlenmeyer flask, 50 mL.
- 7.27 Glass vial, 40 mL.
- 7.28 Cover glass petri dishes for shipping filters.
- 7.29 Fritted glass extraction thimbles.
- 7.30 Pyrex glass tube furnace system for activating silica gel at 180-C under purified nitrogen gas purge for an hour, with capability of raising temperature gradually.

NOTE: Reuse of glassware should be minimized to avoid the risk of cross-contamination. All glassware that is used, especially glassware that is reused, must be scrupulously cleaned as soon as possible after use. Rinse glassware with the last solvent used in it and then with high-purity acetone and hexane. Wash with hot water containing detergent. Rinse with copious amount of tap water and several portions of distilled water. Drain, dry, and heat in a muffle furnace at 400-C for 2 to 4 hours. Volumetric glassware must not be heated in a muffle furnace; rather, it should be rinsed with high-purity acetone and hexane. After the glassware is dry and cool, rinse it with hexane, and store it inverted or capped with solvent-rinsed aluminum foil in a clean environment.

- 8.0 Reagents and Materials**
- 8.1** Ultrapure glass wool, silanized, extracted with methylene chloride and hexane, and dried.
  - 8.2** Ultrapure acid-washed quartz fiber filters for PS-1 Sampler (Pallflex 2500 glass, or equivalent).
  - 8.3** Benzene (Burdick and Jackson, glass-distilled, or equivalent).
  - 8.4** Hexane (Burdick and Jackson, glass-distilled, or equivalent).
  - 8.5** Alumina, acidic - extracted in a Soxhlet apparatus with methylene chloride for 6 hours (minimum of 3 cycles per hour) and activated by heating in a foil-covered glass container for 24 hours at 190-C.
  - 8.6** Silica gel - high-purity grade, type 60, 70-230 mesh; extracted in a Soxhlet apparatus with methylene chloride for 6 hours (minimum of 3 cycles per hour) and activated by heating in a foil-covered glass container for 24 hours at 130-C.
  - 8.7** Silica gel impregnated with 40 percent (by weight) sulfuric acid prepared by adding two parts (by weight) concentrated sulfuric acid to three parts (by weight) silica gel (extracted and activated) and mixing with a glass rod until free of lumps; Stored in a screw-capped glass bottle.
  - 8.8** Graphitized carbon black (Carbopak C or equivalent), surface of approximately 12 m<sup>2</sup>/g, 80/100 mesh - prepared by thoroughly mixing 3.6 grams Carbopak C and 16.4 grams Celite 545(R) in a 40-mL vial and activating at 130-C for six hours; stored in a desiccator.
  - 8.9** Sulfuric Acid, ultrapure, ACS grade, specific gravity 1.84.
  - 8.10** Sodium Hydroxide, ultrapure, ACS grade.
  - 8.11** Native and isotopically labeled PCDD/PCDF isomers for calibration and spiking standards, from Cambridge Isotopes, Cambridge, MA.
  - 8.12** n-decane (Aldrich Gold Label grade [D90-1], or equivalent).
  - 8.13** Toluene (high purity, glass-distilled).
  - 8.14** Acetone (high purity, glass-distilled).
  - 8.15** Filters, quartz fiber - Pallflex 2500 QAST, or equivalent-
  - 8.16** Ultrapure nitrogen gas (Scott chromatographic grade, or equivalent).
  - 8.17** Methanol (chromatographic grade).
  - 8.18** Methylene chloride (chromatographic grade, glass-distilled).
  - 8.19** Dichloromethane/hexane (3:97, v/v), chromatographic grade.
  - 8.20** Hexane/dichloromethane (1: 1, v/v), chromatographic grade.
  - 8.21** Perfluorokerosene (PFK), chromatographic grade.
  - 8.22** Celite 545(R), reagent grade, or equivalent.
  - 8.23** Membrane filters or filter paper with pore sizes less than 25 urn, hexane-rinsed.
  - 8.24** Granular anhydrous sodium sulfate, reagent grade.
  - 8.25** Potassium carbonate-anhydrous, granular, reagent grade.
  - 8.26** Cyclohexane, glass-distilled.
  - 8.27** Tridecane, glass-distilled.
  - 8.28** 2,2,3-trimethylpentane, glass-distilled.
  - 8.29** Isooctane, glass-distilled.

- 8.30 Sodium sulfate, ultrapure, ACS grade.
- 8.31 Polyurethane foam - 3 inches thick sheet stock, polyether type used in furniture upholstery, density 0.022 g/cm<sup>3</sup>.
- 8.32 Concentration calibration solutions (Table 1) - four tridecane solutions containing <sup>13</sup>C<sub>12</sub>-1,2,3,4-TCDD (recovery standard) and unlabeled 2,3,7,8-TCDD at varying concentrations, and <sup>13</sup>C<sub>12</sub>-2,3,7,8-TCDD (internal standard, CAS RN 80494-19-5). These solutions must be obtained from the Quality Assurance Division, U.S. EPA, Environmental Monitoring Systems Laboratory (EMSL-LV), Las Vegas, Nevada, and must be used to calibrate the instrument. However, secondary standards may be obtained from commercial sources, and solutions may be prepared in the analytical laboratory. Traceability of standards must be verified against EPA-supplied standard solutions by procedures documented in laboratory SOPs. Care must be taken to use the correct standard. Serious overloading of instruments may occur if concentration calibration solutions intended for low-resolution MS are injected into the high-resolution MS.
- 8.33 Column performance check mixture dissolved in 1 mL of tridecane from Quality Assurance Division (EMSL-LV). Each ampule of this solution will contain approximately 10 ng of the following components (A) eluting near 2,3,7,8-TCDD and of the first (F) and last-eluting (L) TCDDs, when using the recommended columns at a concentration of 10 pg/uL of each of these isomers:

- unlabeled 2,3,7,8-TCDD
- <sup>13</sup>C<sub>12</sub>-2,3,7,8-TCDD
- 1,2,3,4-TCDD (A)
- 1,4,7,8-TCDD (A)
- 1,2,3,7-TCDD (A)
- 1,2,3,8-TCDD (A)
- 1,3,6,8-TCDD (F)
- 1,2,8,9-TCDD (L)

If these solutions are unavailable from EPA, they should be prepared by the analytical laboratory or a chemical supplier and analyzed in a manner traceable to the EPA performance check mixture designed for 2,3,7,8-TCDD monitoring. Similar mixtures of isotopically labeled compounds should be prepared to check performance for monitoring other specific forms of TCDD that are of interest.

- 8.34 Sample fortification solution - isooctane solution containing the internal standard at a nominal concentration of 10 pg/uL.
- 8.35 Recovery standard spiking solution - tridecane solution containing the isotopically labeled standard (<sup>13</sup>C<sub>12</sub>-2,3,7,8-TCDD and other PCDDs of interest) at a concentration of 10.0 pg/uL.

### 8.36 Field blank fortification solutions - isooctane solutions containing the following:

**Solution A: 10.0 pg/uL of unlabeled 2,3,7,8-TCDD**

**Solution B: 10.0 pg/uL of unlabeled 1,2,3,4-TCDD**

**NOTE:** These reagents and the detailed analytical procedures described herein are designed for monitoring TCDD isomer concentrations of 6.0 pg/m<sup>3</sup> to 37 pg/m<sup>3</sup> each. If ambient concentrations should exceed these levels, concentrations of calibrations and spiking solutions will need to be modified, along with the detailed sample preparation procedures. The reagents and procedures described herein are based on Appendix B of the Protocol for the Analysis of 2,3,7,8-TCDD (Section 2.2.2) combined with the evaluation of the high volume air sampler for PCDD.

### 9.0 Preparation of PUF Sampling Cartridge

- 9.1 The PUF adsorbent is a polyether-type polyurethane foam (density No, 3014 or 0.0225 g/cm<sup>3</sup>) used for furniture upholstery.
- 9.2 The PUF inserts are 6.0-cm diameter cylindrical plugs cut from 3-inch sheet stock and should fit, with slight compression, in the glass cartridge, supported by the wire screen (Figure 1). During cutting, the die is rotated at high speed (e.g., in a drill press) and continuously lubricated with water.
- 9.3 For initial cleanup, the PUF plug is placed in a Soxhlet apparatus and extracted with acetone for 14-24 hours at approximately 4 cycles per hour. When cartridges are reused, 5 % diethyl ether in n-hexane can be used as the cleanup solvent.
- 9.4 The extracted PUF is placed in a vacuum oven connected to a water aspirator and dried at room temperature for approximately 2-4 hours (until no solvent odor is detected).
- 9.5 The PUF is placed into the glass sampling cartridge using polyester gloves. The module is wrapped with hexane-rinsed aluminum foil, placed in a labeled container, and tightly sealed.
- 9.6 At least one assembled cartridge from each batch must be analyzed, as a laboratory blank, using the procedures described in Section 11, before the batch is considered acceptable for field use. A blank level of < 10 ng/plug for single compounds is considered to be acceptable.

### 10.0 Sample Collection

#### 10.1 Description of Sampling Apparatus

- 10.1.1 The entire sampling system is diagrammed in Figure 2. A unit specifically design& for this method is commercially available (Model PS-I- General Metal Works, Inc., Viiage of Cleves, Ohio).

- 10.1.2 The sampling module (Figure 1) consists of a glass sampling cartridge and an air-tight metal cartridge holder. The PUF is retained in the glass sampling cartridge.

## 10.2 Calibration of Sampling System

- 10.2.1 The airflow through the sampling system is monitored by a Venturi/Magnehelic assembly, as shown in Figure 2. Assembly must be audited every six months using an audit calibration orifice, as described in the U.S. EPA High Volume Sampling Method, 40 CFR 50, Appendix B. A single-point calibration must be performed before and after each sample collection, using the procedure described in Section 10.2.2.
- 10.2.2 Prior to calibration, a "dummy" PUF cartridge and filter are placed in the sampling head and the sampling motor is activated. The flow control valve is fully opened and the voltage variator is adjusted so that a sample flow rate corresponding to 110% of the desired flow rate is indicated on the Magnehelic (based on the previously obtained multipoint calibration curve). The motor is allowed to warm up for 10 minutes and then the flow control valve is adjusted to achieve the desired flow rate. The ambient temperature and barometric pressure should be recorded on an appropriate data sheet.
- 10.2.3 The calibration orifice is placed on the sampling head and a manometer is attached to the tap on the calibration orifice. The sampler is momentarily turned off to set the zero level of the manometer. The sampler is then switched on and the manometer reading is recorded after a stable reading is achieved. The sampler is then shut off.
- 10.2.4 The calibration curve for the orifice is used to calculate sample flow from the data obtained in Section 10.2.3, and the calibration curve for the Venturi/Magnehelic assembly is used to calculate sample flow from the data obtained in Section 10.2.2. The calibration data should be recorded on an appropriate data sheet. If the two values do not agree within 10%, the sampler should be inspected for damage, flow blockage, etc. If no obvious problems are found, the sampler should be recalibrated (multipoint) according to the U.S. EPA High Volume Sampling Method (Section 10.2.1).
- 10.2.5 A multipoint calibration of the calibration orifice, against a primary standard, should be obtained annually.

## 10.3 Sample Collection

- 10.3.1 After the sampling system has been assembled and calibrated as described in Sections 10.1 and 10.2, it can be used to collect air samples, as described in Section 10.3.2.
- 10.3.2 The samples should be located in an unobstructed area, at least two meters from any obstacle to air flow. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air.

- 10.3.3 A clean PUP sampling cartridge and quartz filter are removed from sealed transport containers and placed in the sampling head using forceps and gloved hands. The head is tightly sealed into the sampling system. The aluminum foil wrapping is placed back in the sealed container for later use.
- 10.3.4 The zero reading of the Magnehelic is checked. Ambient temperature, barometric pressure, elapsed time meter setting, sampler serial number, filter number, and PUP cartridge number are recorded on a suitable data sheet, as illustrated in Figure 3.
- 10.3.5 The voltage variator and flow control valve are placed at the settings used in Section 10.2.3, and the power switch is turned on. The elapsed time meter is activated and the start time is recorded. The flow (Magnehelic setting) is adjusted, if necessary, using the flow control valve.
- 10.3.6 The Magnehelic reading is recorded every 6 hours during the sampling period. The calibration curve (Section 10.2.4) is used to calculate the flow rate. Ambient temperature and barometric pressure are recorded at the beginning and end of the sampling period.
- 10.3.7 At the end of the desired sampling period, the power is turned off and the filter and PUF cartridges are wrapped with the original aluminum foil and placed in sealed, labeled containers for transport back to the laboratory.
- 10.3.8 The Magnehelic calibration is checked using the calibration orifice, as described in Section 10.2.4. If calibration deviates by more than 10% from the initial reading, the flow data for that sample must be marked as suspect and the sampler should be inspected and/or removed from service.
- 10.3.9 At least one field filter/PUF blank will be returned to the laboratory with each group of samples. A field blank is treated exactly as a sample except that no air is drawn through the filter/PUP cartridge assembly.
- 10.3.10 Samples are stored at 20-C in an ice chest until receipt at the analytical laboratory, after which they are refrigerated at 4-C.

## 11.0 Sample Extraction

- 11.1 Immediately before use, charge the Soxhlet apparatus with 200 to 250 mL of benzene and reflux for 2 hours. Let the apparatus cool, disassemble it, transfer the benzene to a clean glass container, and retain it as a blank for later analysis, if required. After sampling, spike the cartridges and filters with an internal standard (Table 1). After spiking, place the PUP cartridge and filter together in the Soxhlet apparatus (the use of an extraction thimble is optional). (The filter and PUP cartridge are analyzed together in order to reach detection limits, avoid questionable interpretation of the data, and minimize cost.) Add 200 to 250 mL of benzene to the apparatus and relux for 18 hours at a rate of at least 3 cycles per hour.
- 11.2 Transfer the extract to a Kuderna-Danish (K-D) apparatus, concentrate it to 2 to 3 mL, and let it cool. Rinse the column and flask with 5 mL of benzene, collecting the rinsate in the concentrator tube to 2 to 3 mL. Repeat the rinsing and concentration steps twice more. Remove the concentrator tube from the K-D apparatus and

carefully reduce the extract volume to approximately 1 mL with a stream of nitrogen using a flow rate and distance above the solution such that a gentle rippling of the solution surface is observed.

- 11.3 Perform the following column chromatographic procedures for sample extraction cleanup. These procedures have been demonstrated to be effective for a mixture consisting of:

1,2,3,4-TCDD  
1,2,3,4,7,8-HXCDD  
OCDD  
2,3,7,8-TCDD

- 11.3.1 Prepare an acidic silica gel column as follows (Figure 4): Pack a 1 cm x 10 cm chromatographic column with a glass wool plug, a 1-cm layer of Na<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>CO<sub>3</sub> (1:1), 1.0 g of silica gel (Section 8.6), and 4.0 g of 40-percent (w/w) sulfuric acid-impregnated silica gel (Section 8.7). Pack a second chromatographic column (1 cm x 30 cm) with a glass wool plug and 6.0 g of acidic alumina (Section 8.5), and top it with a 1-cm layer of sodium sulfate (Section 8.30). Add hexane to the columns until they are free of channels and air bubbles.
- 11.3.2 Quantitatively transfer the benzene extract (1 mL) from the concentrator tube to the top of the silica gel column. Rinse the concentrator tube with 0.5-mL portions of hexane. Transfer the rinses to the top of the silica gel column.
- 11.3.3 Elute the extract from the silica gel column with 90 mL hexane directly into a Kuderna-Danish concentrator tube. Concentrate the eluate to 0.5 mL, using nitrogen blowdown, as necessary.
- 11.3.4 Transfer the concentrate (0.5 mL) to the top of the alumina column. Rinse the K-D assembly with two 0.5-mL portions of hexane, and transfer the rinses to the top of the alumina column. Elute the alumina column with 18 mL hexane until the hexane level is just below the top of the sodium sulfate. Discard the eluate. Do not let the columns reach dryness (i.e., maintain a solvent "head").
- 11.3.5 Place 30 mL of 20% (v/v) methylene chloride in hexane on top of the alumina column and elute the TCDDs from the column. Collect this fraction in a 50-mL Erlenmeyer flask.
- 11.3.6 Certain extracts, even after cleanup by column chromatography, contain interferences that preclude determination of TCDD at low parts-per-trillion levels. Therefore, a cleanup step is included using activated carbon which selectively retains planar molecules such as TCDDs. The TCDDs are then removed from the carbon by elution with toluene. Proceed as follows: Prepare an 18% Carbopak C/Celite 545(R) mixture by thoroughly mixing 3.6 grams Carbopak C (80/100 mesh) and 16.4 grams Celite 545(R) in a 40-mL vial. Activate the mixture at 130-C for 6 hours, and store it in a desiccator. Cut off a clean 5-mL disposable glass pipet at the 4-mL mark. Insert a plug

of glass wool (Section 8.1) and push it to the 2-mL mark. Add 340 mg of the activated Caropak/Celite mixture followed by another glass wool plug. Using two glass rods, push both glass wool plugs simultaneously toward the Caropak/Celite plug to a length of 2.0 to 2.5 cm. Pre-elute the column with 2 mL of toluene followed by 1 mL of 75:20:5 methylene chloride/methanol/benzene, 1 mL of 1:1 cyclohexane in methylene chloride, and 2 mL of hexane. The flow rate should be less than 0.5 mL per minute. While the column is still wet with hexane, add the entire eluate (30 mL) from the alumina column (Section 11.3.5) to the top of the column. Rinse the Erlenmeyer flask that contained the extract twice with 1 mL of hexane and add the rinsates to the top of the column. Elute the column sequentially with two 1-mL aliquots of hexane, 1 mL of 1:1 cyclohexane in methylene chloride, and 1 mL of 75:20:5 methylene chloride/methanol/benzene. Turn the column upside down and elute the TCDD fraction into a concentrator tube with 6 mL of toluene. Warm the tube to approximately 60-C and reduce the toluene volume to approximately 1 mL using a stream of nitrogen. Carefully transfer the residue into a 1-mL minivial and, again at elevated temperature, reduce the volume to about 100 uL using a stream of nitrogen. Rinse the concentrator tube with 3 washings using 200 uL of 1% toluene in CH<sub>2</sub>Cl<sub>2</sub> each time. Add 50 uL of tridecane and store the sample in a refrigerator until GC/MS analysis is performed.

## 12.0 HRGC/HRMS System Performance Criteria

The laboratory must document that the system performance criteria specified in Sections 12.1, 12.2, and 12.3 have been met before analysis of samples.

### 12.1 GC Column Performance

12.1.1 Inject 2 uL of the column performance check solution (Section 8.33) and acquire selected ion monitoring (SIM) data for m/z 258.930, 319.897, 321.894, and 333.933 within a total cycle time of  $\leq 1$  second. 12.1.2 The chromatographic peak separation between 2,3,7,8-TCDD and the peaks representing any other TCDD isomers must be resolved with a valley of  $\leq 25\%$ , where Valley Percent =  $(x/y)(100)$  x = measured distance from extrapolated baseline to minimum of valley; and y = the peak height of 2,3,7,8-TCDD.

Note: It is the responsibility of the laboratory to verify the conditions suitable for the appropriate resolution of 2,3,7,8-TCDD from all other TCDD isomers. The column performance check solution also contains the TCDD isomers eluting first and last under the analytical conditions specified in this

protocol, thus defining the retention time window for total TCDD determination. The peaks representing 2,3,7,8-TCDD, and the first and last eluting TCDD isomers must be labeled and identified.

## 12.2 Mass Spectrometer Performance

- 12.2.1 The mass spectrometer must be operated in the electron (impact) ionization **mode**. **Static** mass resolution of at least 10,000 (10% valley) must be demonstrated before any analysis of a set of samples is performed (Section 12.2.2). **Static** resolution checks must be performed at the beginning and at the end of each 12-hour period of **operation**. However, it is recommended that a visual check (e.g., not documented) of the static resolution be made using the peak matching unit before and after each analysis.
- 12.2.2 Chromatography time for TCDD may exceed the long-term mass stability of the mass **spectrometer**; therefore, mass drift correction is mandatory. A reference compound (high boiling **perfluorokerosene** (PFK) is recommended) is introduced into the mass spectrometer. An acceptable lock mass ion at any mass between  $m/z$  250 and  $m/z$  334 ( $m/z$  318.979 from PFK is recommended) must be used to monitor and **correct** mass **drifts**.

**NOTE:** Excessive **PFK** may cause background noise problems and **contamination** of the source, resulting in an increase in "downtime" for source cleaning. Using a **PFK** molecular leak, tune the instrument to meet **the** minimum required mass resolution of 10,000 (10% valley) at  $m/z$  254.986 (or any other mass reasonably close to  $m/z$  259). Calibrate the voltage sweep at least across the mass range  $m/z$  259 to  $m/z$  344 and verify that  $m/z$  330.979 from **PFK** (or any other mass close to  $m/z$  334) is measured within +5 ppm (i.e., 1.7 mmu). Document the mass resolution by recording the peak profile of the **PFK** reference peak  $m/z$  318.979 (or any other reference peak at a mass close to  $m/z$  320/322). The format of the **peak** profile representation must allow manual **determination** of the resolution; i.e., the horizontal axis must be a calibrated mass scale (mmu or ppm per division). The result of the **peak** width measurement (performed at 5 percent of the maximum) must appear on the hard copy and cannot exceed 3.19 mmu or 100 ppm.

## 12.3 Initial Calibration

Initial calibration is required before any samples are analyzed for 2,3,7,8-TCDD. Initial calibration is also required if any routine calibration does not meet the required criteria listed in Section 12.6.

- 12.3.1 All **concentration** calibration solutions listed in Table 1 must be utilized for the initial calibration.

- 12.3.2 Tune the instrument with PFK as described in Section 12.2.2.
- 12.3.3 Inject 2  $\mu\text{L}$  of the column performance check solution (Section 8.33) and acquire SIM mass spectral data for  $m/z$  258.930, 319.897, 321.894, 331.937, and 333.934 within a total cycle time of  $\leq 1$  second. The laboratory must not perform any further analysis until it has been demonstrated and documented that the criterion listed in Section 12.1.2 has been met.
- 12.3.4 Using the same GC (Section 12.1) and MS (Section 12.2) conditions that produced acceptable results with the column performance check solution, analyze a 2- $\mu\text{L}$  aliquot of each of the 5 concentration calibration solutions in triplicate with the gas chromatographic operating parameters shown in Table 2.

12.3.4-1 Total cycle time for data acquisition must be  $\leq 1$  second. Total cycle time includes the sum of all the dwell times and voltage reset times.

12.3.4.2 Acquire SIM data for the following selected

characteristic ions:

$m/z$	Compound
-------	----------

258.930	TCDD - COC1
---------	-------------

319.897	unlabeled TCDD
---------	----------------

321.894	unlabeled TCDD
---------	----------------

331.937	$^{13}\text{C}_{12}$ -2,3,7,8-TCDD, $^{13}\text{C}_{12}$ -1,2,3,4-TCDD
---------	--

333.934	$^{13}\text{C}_{12}$ -2,3,7,8-TCDD, $^{13}\text{C}_{12}$ -1,2,3,4-TCDD
---------	--

12.3.4.3 The ratio of integrated ion current for  $m/z$  319.897 to  $m/z$  321.894 for 2,3,7,8-TCDD must be between 0.67 and 0.87 ( $\pm 13\%$ ).

12.3.4.4 The ratio of integrated ion current for  $m/z$  331.937 to  $m/z$  333.934 for  $^{13}\text{C}_{12}$ -2,3,7,8-TCDD and  $^{13}\text{C}_{12}$ -1,2,3,4-TCDD must be between 0.67 and 0.87.

12.3.4.5 Calculate the relative response factor for unlabeled 2,3,7,8-TCDD [RRF(I)] relative to  $^{13}\text{C}_{12}$ -2,3,7,8-TCDD and for labeled  $^{13}\text{C}_{12}$ -2,3,7,8-TCDD [RRF(II)] relative to  $^{13}\text{C}_{12}$ -1,2,3,4-TCDD as follows:

$$\text{RRF(I)} = \frac{A(x) * Q(\text{IS})}{Q * A(\text{IS})}$$

$$\text{RRF(II)} = \frac{A(\text{IS}) * Q(\text{RS})}{Q(\text{IS}) * A(\text{RS})}$$

where:

- A(x) = sum of the integrated abundances of m/z 319.897 and m/z 321.894 for unlabeled 2,3,7,8-TCDD.
- A(IS) = sum of the integrated abundances of m/z 331.937 and m/z 312-2,3,7,8-TCDD.
- A(RS) = sum of the integrated abundances for m/z 331.937 and m/z 333.934 for 13C12-1,2,3,4-TCDD.
- Q(IS) = quantity (pg) of 13C12-2,3,7,8-TCDD injected.
- Q(RS) = quantity (pg) of 13C12-1,2,3,4-TCDD injected.
- Q(x) = quantity (pg) of unlabeled 2,3,7,8-TCDD injected.

12.4 Criteria for Acceptable Calibration The criteria listed below for acceptable calibration must be met before analysis of any sample is performed.

- 12.4.1 The percent relative standard deviation (RSD) for the response factors from each of the triplicate analyses for both unlabeled and 13C12-2,3,7,8-TCDD must be less than +/-20%.
- 12.4.2 The variation of the five mean RRFs for unlabeled 2,3,7,8-TCDD obtained from the triplicate analyses must be less than +/-20% RSD.
- 12.4.4 SIM traces for 13C12-2,3,7,8-TCDD must present a signal-to-noise ratio  $\geq 10$  for 333.934.
- 12.4.5 Isotopic ratios (Sections 12.3.4.3 and 12.3.4.4) must be within the allowed range.

NOTE: If the criteria for acceptable calibration listed in Sections 12.4.1 and 12.4.2 have been met, the RRF can be considered independent of the analyte quantity for the calibration concentration range. The mean RRF from five triplicate determinations for unlabeled 2,3,7,8-TCDD and for 13C12-2,3,7,8-TCDD will be used for all calculations until routine calibration criteria (Section 12.6) are no longer met. At such time, new mean RRFs will be calculated from a new set of five triplicate determinations.

## 12.5 Routine Calibration

Routine calibration must be performed at the beginning of each 12-hour period after successful mass resolution and GC column performance check runs.

- 12.5.1 Inject 2 uL of the concentration calibration solution (Section 8.32) that contains 5.0 pg/uL of unlabeled 2,3,7,8-TCDD, 10.0 pg/uL of 13C12-2,3,7,8-TCDD, and 5.0 pg/uL 13C12-1,2,3,4-TCDD. Using the same GC/MS/DS conditions as in Sections 12.1, 12.2, and 12.3, determine and document acceptable calibration as provided in Section 12.6.

12.6 Criteria for Acceptable **Routine** Calibration. The following criteria must be met before further analysis is performed. If these criteria **are** not met, corrective action must be taken and the instrument must be recalibrated.

12.6.1 The measured RRF for unlabeled **2,3,7,8-TCDD** must be within +/-20 percent of the mean values established (Section 12.3.4.5) by **triplicate** analyses of concentration calibration solutions.

12.6.2 The **measured RRF** for **13C12-2,3,7,8-TCDD** must **be** within +/-20 percent of the mean value established by triplicate analyses of concentration calibration solutions (Section **12.3.4.5**).

12.6.3 Isotopic ratios (Sections 12.3.4.3 and 12.3.4.4) must be within the allowed range.

12.6.4 If one of the above criteria is not satisfied, a second attempt can be made before repeating the entire **initialization** process (Section 12.3).

NOTE: An initial calibration must be **carried** out whenever any **HRCC** solution is replaced.

### 13.0 Analytical Procedures

13.1 Remove the **sample** extract or **blank** from storage, allow it to warm to ambient laboratory temperature, and add 5 **uL** of recovery standard solution. With a stream of dry, purified nitrogen, reduce the **extract/blank** volume to 20 **uL**.

13.2 Inject a **2-uL aliquot** of the extract into the GC, which should be operating under the conditions previously used (Section 12.1) to produce acceptable results with the performance check solution.

13.3 Acquire **SIM** data using the same acquisition time and MS operating conditions previously used (Section 12.3.4) to determine the relative response factors for the following selected characteristic ions:

<b>m/z</b>	<b>Compound</b>
258.930	TCDD - <b>COC1</b> (weak at detection limit level)
319.897	unlabeled TCDD
321.894	<b>unlabeled</b> TCDD
331.937	<b>13C12-2,3,7,8-TCDD, 13C12-1,2,3,4-TCDD,</b>
333.934	<b>13C12-2,3,7,8-TCDD, 13C12-1,2,3,4-TCDD,</b>

### 13.4 Identification Criteria

13.4.1 The retention time (**RT**) (at maximum **peak** height) of the sample component m/z 319.897 must be within -1 to **+3** seconds of the retention time of the **peak** for the isotopically labeled internal standard at m/z 331.937 to **attain** a

positive identification of **2,3,7,8-TCDD**. Retention times of other tentatively identified **TCDDs** must fall within the RT window established by analyzing the column performance check solution (Section 12.1). Retention times are required for all chromatograms.

- 13.4.2 The ion current responses for m/z 258.930, 319.897 and 321.894 must reach their maxima simultaneously ( $\pm 1$  scan), and **all** ion current intensities must be  $\geq 2.5$  times noise level for positive **identification** of a TCDD.
- 13.4.3 The integrated ion current at **m/z** 319.897 must **be** between 67 and 87 percent of the ion current response at **m/z** 321.894.
- 13.4.4 The integrated ion current at **m/z** 331.937 must **be** between 67 and 87 percent of the ion current response at m/z 333-934.
- 13.4.5 The integrated ion currents for m/z 331.937 and 333.934 must reach their maxima within  $\pm 1$  scan.
- 13.4.6 The recovery of the internal standard **<sup>13</sup>Cl<sub>2</sub>-2,3,7,8-TCDD** must be between 40 and 120 percent.

#### 14.0 Calculations

- 14.1 Calculate the concentration of **2,3,7,8-TCDD** (or any other TCDD isomer) using the **formula**:

$$c(x) = \frac{A(X) * Q(IS)}{A(IS) * V * RRF(I)}$$

where:

- C(X)** = quantity (**pg**) of unlabeled **2,3,7,8-TCDD** (or any other unlabeled TCDD isomer) present.
- A(X)** = sum of the **integrated** ion abundances determined for m/z 319.897 and 321.894.
- A(IS)** = sum of the **integrated** ion abundances determined for m/z 331.937 and 333.934 of **<sup>13</sup>Cl<sub>2</sub>-2,3,7,8-TCDD** (IS = **internal standard**).
- Q(IS)** = quantity (**pg**) of **<sup>13</sup>Cl<sub>2</sub>-2,3,7,8-TCDD** added to the sample before extraction (**QIS = 500 pg**)
- v** = volume (m<sup>3</sup>) of air sampled.
- RRF(I)** = **Calculated** mean relative response factor for unlabeled **2,3,7,8-TCDD** relative to **<sup>13</sup>Cl<sub>2</sub>-2,3,7,8-TCDD**. **This** value represents the grand mean of the **RRF(I)s** obtained in Section 12.3.4.5.

- 14.2 Calculate the recovery of the internal standard **<sup>13</sup>Cl<sub>2</sub>-2,3,7,8-TCDD**, measured in the sample extract, using the formula:

$$\text{Internal standard percent recovery} = \frac{I(\text{AS}) * Q(\text{RS})}{A(\text{RS}) * \text{RRF}(\text{II}) * Q(\text{IS})} * 100$$

where:

**A(RS)** = sum of the integrated ion abundances determined for m/z 331.937 and 333.934 of **<sup>13</sup>Cl<sub>2</sub>-1,2,3,4-TCDD** (**RS** = recovery standard).

**Q(RS)** = quantity (**pg**) of **<sup>13</sup>Cl<sub>2</sub>-1,2,3,4-TCDD** added to the sample residue before **HRGC-HRMS** analysis (**QRS** = 500 pg)

**RRF(II)** = Calculated mean relative response factor for labeled **<sup>13</sup>Cl<sub>2</sub>-2,3,7,8-TCDD**. This value represents the grand mean of the **RRF(II)**s calculated in Section 12.3.4.5.

**A(IS)** and

**Q(IS)** = **same definitions** as above (Section 14.1)

#### 14.3 Total TCDD Concentration

- 14.3.1. **All** positively identified isomers of TCDD must be within the RT window and meet **all identification** criteria listed in Sections 13.4.2, 13.4.3, and 13.4.4. Use the expression in Section 14.1 to calculate the concentrations of the other TCDD isomers, with C<sub>x</sub> becoming the concentration of any unlabeled TCDD isomer.

#### 14.4 Estimated Detection Limit

- 14.4.1 For samples in which no unlabeled **2,3,7,8-TCDD** was detected, calculate the estimated minimum detectable concentration. The background **area** is determined by integrating the ion abundances for m/z 319.897 and 321.894 in the appropriate region and relating that height area to an estimated concentration that would produce that product area. Use the formula:

$$CE = \frac{(2.5) * A(x) * Q(\text{IS})}{A(\text{IS}) * \text{RRF}(\text{I}) * W}$$

where:

- C(E)** = estimated concentration of **unlabeled 2,3,7,8-TCDD** required to produce A<sub>x</sub>.  
**A(x)** = sum of integrated ion abundance for m/z 319.897 and 321.894 in the same group of **>=25** scans used to **measure AIS**.

**A(IS)** = sum of integrated ion abundance for the appropriate ion characteristic of the internal standard, m/z 331.937 and m/z 333.934.

**QIS**, **RRF(I)**, and **V** retain the definitions previously stated in Section 14.1. Alternatively, if **peak** height measurements are used for **quantification**, measure the estimated detection limit by the **peak** height of the noise in the TCDD RT window.

14.5 The relative percent difference (**RPD**) is calculated as follows:

$$\text{RPD} = \frac{(\text{S1} - \text{S2})}{(\text{Mean Concentration}) (\text{S1} + \text{S2})/2} = \frac{(\text{S1} - \text{S2})}{(\text{S1} + \text{S2})} * 100$$

**S1** and **S2** represent sample and duplicate sample results.

14.6 The total sample volume (**Vm**) is calculated from the periodic flow readings (Magnehelic) taken in Section 10.3.6 using the following equation:

$$V(m) = \frac{Q1 + Q2 \dots QN}{N} * \frac{T}{1000}$$

where:

**V(m)** = total sample volume (m3).

**Q1 Q2...QN** = flow rates determined at the beginning, end, and intermediate points during sampling (**L/minute**).

**N** = number of data points averaged.

**T** = elapsed sampling **time** (minutes).

14.7 The concentration of compound in the sample is calculated using **the** following equation:

$$V(s) = V(m) * \frac{P(A)}{760} * \frac{298}{273 + t(a)}$$

where:

**V(s)** = total sample volume (m3) at 25-C and 760 mm Hg **pressure**.

**V(m)** = total sample **flow** (m3) under ambient conditions.

**P(A)** = ambient pressure (mm Hg).

**t(a)** = ambient temperature (-C).

14.8 The concentration of compound in the sample is calculated using the following equation:

$$C(A) = \frac{A * V(E)}{V(i) * V(s)}$$

where:

- C(A) = concentration (**ug/m3**) of **analyte** in the sample.  
A = calculated amount of material determined by **HRGC/HRMS**.  
V(i) = volume (**uL**) of **extract** injected.  
V(E) = final volume (**mL**) of extract.  
V(s) = total volume (m3) of air samples **corrected** to standard conditions.

## 15.0 Performance Criteria and Quality Assurance

This section summarizes required quality assurance (QA) measures and provides guidance concerning performance criteria that should be achieved within each laboratory\*

### 15.1 standard **Operating Procedures** (SOPS)

- 15.1.1 Users should generate **SOPs** describing the following activities in their laboratory: 1) assembly, calibration and operation of the sampling system with make and model of equipment **used**; 2) preparation, purification, storage, and handling of sampling cartridges and filters; 3) assembly, calibration and operation of the **HRGC/HRMS** system with make and model of equipment used; 4) all aspects of data recording and processing, including lists of computer hardware and software used.
- 15.1.2 **SOPs** should provide specific **stepwise** instructions and should be readily available to and **understood** by the laboratory personnel conducting the work.

### 15.2 Process, Field, and Solvent Blanks

- 15.2.1 One PUF cartridge and filter from each batch of approximately 20 should be analyzed, without shipment to the field, for the compounds of interest to serve as process blank.
- 15.2.2 **During** each sampling episode, at **least** one **PUF** cartridge and filter should be shipped to the field and returned, without **drawing** air through the sampler, to **serve** as a field blank.
- 15.2.3 During the analysis of each batch of samples, at least one solvent process blank (all steps conducted but no PUF **cartridge** or filter included) should be carried through the procedure and analyzed.

TABLE 1. COMPOSITION OF CONCENTRATION CALIBRATION SOLUTIONS

Recovery Standards 13C12-1,2,3,4-TCDD	Analyte 2,3,7,8-TCDD	Internal Standard 13C12-2,3,7,8-TCDD
HRCC1	2.5 pg/uL	10.0 pg/uL
HRCC2	5.0 pg/uL	10.0 pg/uL
HRcc3	10.0 pg/uL	10.0 pg/uL
HRcc4	20.0 pg/uL	10.0 pg/uL
HRCC5	40.0 pg/uL	10.0 pg/uL
Sample Fortification Solution 5.0 pg/uL of 13C12-2,3,7,8-TCDD		
Recovery Standard Spiking Solution 100 pg/uL 13C12-1,2,3,4-TCDD		
Field Blank Fortification Solutions A) 4.0 pg/uL of unlabeled 2,3,7,8-TCDD B) 5.0 pg/uL of unlabeled 1,2,3,4-TCDD		

TABLE 2. RECOMMENDED GC OPERATING CONDITIONS

Column coating	SP-2330 (SP 2331)	CP-SIL 88
Film thickness	0.20 um	0.22 um
Column dimensions	60 m x 0.24 mm	50 m x 0.22 mm
Helium linear velocity	28-29 cm/sec at 240-C	28-29 cm/sec at 240-C
Initial temperature	200-c	190-c'
Initial time	4 min	3 min
Temperature program	200-C to 250-C at 4-C/min	190-C to 240-C at 5-C/min

ANNEX E-4

METHOD #: TO-13

REVISION #: 1.0 (June 1987)

TITLE: The Determination Of **Benzo(a)pyrene [b(a)p]** And Other Polynuclear Aromatic Hydrocarbons (**PAHs**) In Ambient Air Using Gas **Chromatographic** (GC) And High Performance Liquid **Chromatographic (HPLC)** Analysis

ANALYTE:	CAS #
PAH	
Acenaphthene	83-32-9
Acenaphthylene	
<b>Anthracene</b>	120-12-7
<b>Benzo(a)anthracene</b>	56-55-3
<b>Benzo(a)pyrene</b>	50-32-8
<b>Benzo(b)fluoranthene</b>	205-99-2
<b>Benzo(e)pyrene</b>	192-97-2
<b>Benzo(g,h,i)perylene</b>	191-24-2
<b>Benzo(k)fluoranthene</b>	207-08-g
<b>Chrysene</b>	218-01-g
<b>Dibenzo(a,h)anthracene</b>	53-70-3
<b>Fluoranthene</b>	206-44-o
<b>Fluorene</b>	86-73-7
<b>Indeno(1,2,3-cd)pyrene</b>	193-39-5
Naphthalene	91-20-3
<b>Phenanthrene</b>	85-01-S
<b>Pyrene</b>	129-00-0

INSTRUMENTATION: **HPLC, GC, GC/MS**

## OUTLINE

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### 17.3 Sample Conversion from ng/m<sup>3</sup> to ppbv

## 18.0 Bibliography

### METHOD

#### 1.0 scope

- 1.1 **Polynuclear** aromatic hydrocarbons (**PAHS**) have **received** increased attention in recent years **in** air pollution studies because some of these compounds are highly **carcinogenic** or mutagenic. In particular, **benzo[a]pyrene (B[a]P)** has been **identified** as being highly carcinogenic. To understand the extent of human exposure to **B[a]P**, and other **PAHs**, a reliable sampling and analytical **method** has been established. This document describes a sampling and analysis procedure for **B[a]P** and other **PAHs** involving a combination quartz filter/adsorbent **cartridge** with subsequent analysis by gas chromatography (GC) with flame ionization (**FI**) and mass **spectrometry** (MS) detection (**GC/FI** and GUMS) or high resolution liquid chromatography (**HPLC**). The **analytical** methods are a **modification** of EPA Test Method 610 and 625, Methods for Organic **Chemical** Analysis of Municipal and Industrial Wastewater, and Methods 8000, 8270, and 8310, Test Methods for Evaluation of Solid Waste.
- 1.2 Fluorescence methods were among the very **first** methods used for detection of **B[a]P** and other **PAHS** as a carcinogenic constituent of coal tar (1-7). Fluorescent methods are capable of measuring **sub-nanogram** quantities of **PAHs**, but tend to be fairly non-selective. The **normal spectra obtained** tended to be intense and lacked resolution. Efforts **to** overcome this **difficulty** led to the use of ultraviolet (**W**) absorption spectroscopy as the detection method coupled with pre-specified techniques involving liquid chromatography (**LC**) and thin layer chromatography (TLC) to isolate **specific PAHs**, particularly **B[a]P** (8). As with fluorescence spectroscopy, the individual spectra for various **PAHS** are unique, although portions of spectra for different compounds may be the same. **As** with fluorescence techniques, the possibility of spectra-overlap required complete **separation** of sample components to insure accurate measurement of component levels. Hence, the use of **W** absorption coupled with pre-speciation, involving LC and TLC and fluorescence spectroscopy has declined and is now being replaced **with** the more sensitive high performance liquid chromatography (9) with **W/fluorescence** detection and highly sensitive and specific gas **chromatograph** With either flame ionization detector or coupled with mass **spectroscopy** (10-11).
- 1.3 The choice of GC and HPLC as the recommended procedures for analysis of **B[a]P** and other **PAHs** are influenced by their sensitivity and selectivity, along with their ability to analyze complex samples. This method provides for both GC and **HPLC** approaches to the determination of **B[a]P** and other **PAHs** in the **extracted** sample.
- 1.4 The analytical methodology is well **defined**, but the sampling procedures can reduce the validity of the **analytical** results. Recent studies (12-15) have indicated that non-volatile **PAHs** (vapor pressure **< 10<sup>-3</sup>** mm Hg) may be trapped on the filter, but

post-collection volatilization problems may distribute the **PAHs** down **stream** of the **filter** to the back-up adsorbent. A wide variety of adsorbents such as **Tenax GC**, **XAD-2 resin** and **polyurethane foam (PUP)** have been used to sample **B[a]P** and other **PAH vapors**. All **adsorbents** have demonstrated high collection efficiency for **B[a]P** in particular. In general, **XAD-2 resin** has a higher **collection** efficiency (**16-17**) for volatile **PAHs** than **PUF**, as well as a higher retention efficiency. However, **PUP** cartridges are easier to **handle in** the field and maintain **better** flow characteristics during sampling. Likewise, **PUP** has **demonstrated** its capability **in** sampling **organochlorine** pesticides and **polychlorinated** biphenyls (Compendium Methods **TO4** and **TO10** respectively), and **polychlorinated dibenzo-p-dioxins** (Compendium Method **TO9**). However, **PUF** has demonstrated a lower recovery efficiency and storage capability for naphthalene and **B[a]P**, respectively, than **XAD-2**. There have been no significant losses of **PAHs**, up to 30 days of storage at O-C, using **XAD-2**. It also **appears** that **XAD-2 resin** has a higher collection efficiency for volatile **PAHs** than **PUF**, as well as a higher retention efficiency for both volatile and reactive **PAHs**. Consequently, while the literature cites weaknesses and strengths of using either **XAD-2** or **PUF**, this method covers both the **utilization** of **XAD-2** and **PUF** as the adsorbent to address post collection volatilization problems associated with **B[a]P** and other reactive **PAHs**.

- 1.5 This method covers the determination of **B[a]P specifically** by both **GC** and **HPLC** and enables the qualitative and quantitative analysis of the other **PAHs**. They are:

Acenaphthene	<b>Benzo(k)fluoranthene</b>
Acenaphthylene	<b>Chrysene</b>
<b>Anthracene</b>	<b>Dibenzo(a,h)anthracene</b>
<b>Benzo(a)anthracene</b>	<b>Fluoranthene</b>
<b>Benzo(a)pyrene</b>	Fluorene
<b>Benzo(b)fluoranthene</b>	<b>Indeno(1,2,3-cd)pyrene</b>
<b>Benzo(e)pyrene</b>	<b>Naphthalene</b>
<b>Benzo(g,h,i)perylene</b>	<b>Phenanthrene</b>
	Pyrene

The **GC** and **HPLC** methods **are** applicable to the determination of **PAHs** compounds involving two-member rings or higher. **NitroPAHs** have not been fully evaluated using this procedure; therefore, they are not included in this method. When either of the methods are used to **analyze** unfamiliar samples for any or **all** of the compounds listed above, compound **identification** should **be** supported by both techniques.

- 1.6 With **careful** attention to reagent purity and optimized **analytical** conditions, the detection limits for **GC** and **HPLC methods** range from 1 ng to 10 pg which represents detection of **B[a]P** and other **PAHs** in filtered **air** at levels below 100 **pg/m<sup>3</sup>**. To obtain this detection limit, at least 100 **m<sup>3</sup>** of **air** must be sampled.

## 2.0 Applicable Documents

### 2.1 ASTM standards

- 2.1.1 **Method D1356** - Definitions of Terms Relating to Atmospheric Sampling and Analysis.
- 2.1.2 Method **E260** - Recommended Practice for General Gas Chromatography Procedures.
- 2.1.3 **Method E355** - Practice for Gas Chromatography Terms and Relationships.
- 2.1.4 Method E682 - Practice for Liquid Chromatography Terms and Relationships.
- 2.1.5 Method D-1605-60 - Standard Recommended Practices for Sampling Atmospheres for Analysis of Gases and Vapors.

### 2.2 Other Documents

- 2.2.1 Existing Procedures (18-25)
- 2.2.2 Ambient Air Studies (26-28)
- 2.2.3 U.S. EPA Technical Assistance Document (29-32)
- 2.2.4 General Metal Works Operating Procedures for Model PS-1 Sampler, General Metal Works, Inc., Village of Cleves, Ohio.

## 3.0 Summary of Method

- 3.1 Filters and adsorbent **cartridges** (containing XAD-2 or **PUF**) are **cleaned in** solvents and vacuum-dried. The **filters** and adsorbent **cartridges** are stored in screw-capped jars wrapped in aluminum foil (or otherwise protected from light) before careful installation on a modified high volume sampler.
- 3.2 Approximately 325 m<sup>3</sup> of ambient air is drawn through the **filter** and adsorbent **cartridge** using a calibrated General Metal Works Model PS-1 Sampler, or equivalent (**breakthrough** has not shown to be a problem with sampling volumes of 325 m<sup>3</sup>).
- 3.3 The amount of air sampled through the filter and adsorbent cartridge is recorded, \*and the **filter** and **cartridge** are placed in an appropriately labeled container and shipped along with blank filter and adsorbent cartridges to the **analytical** laboratory for analysis.
- 3.4 The **filters** and adsorbent cartridge are extracted by **Soxhlet** extraction with appropriate solvent. The extract is concentrated by Kuderna-Danish (**K-D**) evaporator, followed by silica gel clean-up using column chromatography to remove potential interferences prior to analysis.
- 3.5 The eluent is further concentrated-by-K-D evaporator, then analyzed by either gas chromatography equipped with **FI**, or MS detection or high performance liquid chromatography (**HPLC**). The analytic&l system is **verified** to be operating properly and calibrated with five concentration calibration solutions, each analyzed in triplicate.

- 3.6 A preliminary analysis of the sample extract is performed to check the system performance and to ensure that the samples are within the calibration range of the instrument. If necessary, recalibrate the instrument, adjust the amount of the sample injected, adjust the calibration solution concentration, and adjust the data processing system to reflect observed retention times, etc. The **samples** and the blanks are analyzed and used (along with the amount of air sampled) to calculate the concentration of **B[a]P** in ambient air.
- 3.8 Other **PAHs** can be determined both qualitatively and quantitatively through optimization of the GC or **HPLC procedures**.

#### 4.0 **Significance**

- 4.1 Several documents have been published which describe sampling and analytical approaches for **benzo[a]pyrene** and other **PAHs**, as outlined in Section 2.2. The attractive features of these methods have **been** combined **in** this procedure. This method has been validated in the laboratory; however, one must use caution when employing it for specific applications.
- 4.2 The relatively low level of **B[a]P** and other **PAHs** in the environment requires use of high volume (~ 6.7 cfm) **sampling** techniques to **acquire** sufficient sample for analysis. However, the volatility of certain **PAHs** prevents efficient collection on filter media alone. Consequently, this method utilizes both a filter and a backup adsorbent cartridge which provide for efficient collection of most **PAHs**.

#### 5.0 **Definitions**

Definitions used in this document and in any user-prepared standard operating procedures (SOPs) should be consistent with **ASTM Methods D1356, D1605-60, E260, and E255**. All abbreviations and symbols are defined within this document at point of use.

- 5.1 Sampling **efficiency** (SE) - ability of the **sampling** medium to trap vapors of interest. **%SE** is the percentage of the **analyte** of interest collected and retained by the sampling medium when it is introduced as a vapor in air or nitrogen into the air sampler and the **sampler** is operated under normal conditions for a period of time equal to or greater than that **required** for the intended use.
- 5.2 Retention time (**RT**) - time to elute a specific chemical from a chromatographic column. For a **specific** tier gas flow rate, RT is **measured** from the time the chemical is injected into the gas **stream** until it **appears** at the detector.
- 5.3 High Performance Liquid Chromatography - an **analytical** method based on separation of compounds of a liquid mixture through a liquid chromatographic column and **measuring** the separated components with a suitable detector.

- 5.4 Gradient elution - defined as increasing the strength of the mobile phase during a **chromatographic** analysis. The net effect of gradient elution is to **shorten** the retention time of compounds strongly retained on the analytical column. Gradient elution may be **stepwise** or continuous.
- 5.5 Method detection limit (**MDL**) - the minimum concentration of a substance that can be measured and reported with **confidence** and that the value is above zero.
- 5.6 Kuderna-Danish **apparatus** - the Kuderna-Danish (**KD**) apparatus is a system for concentrating materials **dissolved** in volatile solvents.
- 5.7 Reverse phase liquid **chromatography** - reverse phase liquid **chromatography** involves a non-polar adsorbent (C-18, ODS) coupled with a polar solvent to separate non-polar compounds.
- 5.8 **Guard** column - guard columns in **HPLC** are **usually** short (5cm) columns attached after **the** injection port and before the analytical column to prevent particles and strongly retained compounds from accumulating on the analytical column. The guard column should always be the same stationary phase as the analytical column and is used to extend the life of the **analytical** column.
- 5.9 **MS-SIM** - the GC is coupled to a select ion mode (**SIM**) detector where the instrument is **programmed** to acquire data for only the target compounds and to disregard all others. This is performed using **SIM** coupled to retention time discriminators. The **SIM** analysis procedure provides quantitative results.
- 5.10 Sublimation - Sublimation is the direct passage of a substance from the solid state to the gaseous state and back into the solid form without at any time appearing in the liquid state. Also applied to the conversion of solid to vapor without the later return to solid state, and to a conversion directly **from** the vapor phase to the solid state.
- 5.11 Surrogate standard - A **surrogate** standard is a **chemically** inert compound (not expected to occur in the environmental sample) which is added to each sample, blank and matrix spiked sample before extraction and analysis. The recovery of the surrogate standard is used to monitor unusual matrix effects, gross sample processing **errors**, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within acceptable limits.
- 5.12 Retention **time** window - Retention time window is determined for each **analyte** of interest and is the time from injection to elution of a specific chemical from a **chromatographic** column. **The** window is determined by three injections of a single component standard over a **72-hr** period **as** plus or minus three times the standard deviation of the absolute retention time for that **analyte**.
- 6.0 Interferences
- 6.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing **hardware** that result in discrete artifacts and/or elevated baselines in the detector **profiles**. All of these materials must be routinely **demonstrated** to be free **from** interferences under the conditions of the analysis by **running** laboratory reagent blanks.

- 6.1.1 Glassware must be scrupulously cleaned (33). Clean all glassware as soon as possible after use by rinsing With the last solvent used in it. This should be followed by detergent washing with hot water, and rinsing with tap water and reagent water. It should then be **drained** dry, solvent rinsed with acetone and **spectrographic** grade **hexane**. After drying and rinsing, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other **contaminants**. Glassware should be stored inverted or **capped** with aluminum foil.
- 6.1.2 The use of high purity water, **reagents** and solvents helps to minimize interference problems. **Purification** of solvents by distillation in all-glass systems may be required.
- 6.1.3 Matrix interferences may be caused by contaminants that are **coextracted** from the sample. Additional clean-up by column chromatography may be required (see **Section** 12.4).
- 6.2 The extent of interferences that may be encountered using liquid **chromatographic** techniques has not been fully assessed. Although GC and HPLC conditions described allow for unique resolution of the specific PAH compounds covered by this method, other PAH compounds may interfere. The use of column chromatography for sample clean-up prior to GC or **HPLC** analysis **will** eliminate most of these interferences. **The analytical** system must, however, be routinely demonstrated to be free of internal contaminants such as contaminated solvents, glassware, or other reagents which may lead to method interferences. A laboratory **reagent** blank is run for each batch of reagents used to **determine** if reagents **are** contaminant-free.
- 6.3 Although **HPLC** separations have **been** improved by recent advances in column technology and instrumentation, problems may occur with baseline noise, baseline drift, peak resolution and changes in sensitivity. Problems affecting overall system performance **can arise** (34). The User is **encouraged** to develop a standard operating procedure (SOP) manual **specific** for his laboratory to minimize problems affecting overall system performance.
- 6.4 Concern during sample transport and analysis is mentioned. Heat, ozone, NO<sub>2</sub> and ultraviolet (**W**) light may cause sample degradation. These problems should be addressed as **part** of the user prepared standard operating procedure manual. Where possible, incandescent or UV-shield fluorescent lighting should be used during analysis.
- 7.0 Safety
- 7.1 The toxicity or **carcinogenicity** of each reagent used in this method has not **been** precisely **defined**; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals

- specified in this method. A reference **file** of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been **identified** for the analyst (35-37).
- 7.2 **Benzo[a]pyrene** has been tentatively classified as a known or suspected, human or mammalian carcinogen. Many of the other **PAHS** have been classified as carcinogens. Care must be exercised when working with these substances. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses **this method** to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. The user should be thoroughly familiar with the **chemical** and physical properties of targeted substances (Table 1 .0 and Figure 1 .0).
- 7.3 Treat all selective **polynuclear aromatic hydrocarbons** as carcinogens. Neat compounds should be weighed in a glove box. Spent samples and unused standards are toxic waste and should be disposed according to regulations. Regularly check counter tops and equipment with "black light" for fluorescence as an indicator of contamination.
- 7.4 Because the sampling configuration (filter **and** backup adsorbent) has demonstrated greater than 95 % collection efficiency for targeted **PAHs**, no field recovery evaluation will occur as part of this procedure.
- 8.0 Apparatus
- 8.1 Sample Collection
- 8.1.1 General Metal Works (**GMW**) Model PS-1 Sampler, or equivalent [General Metal Works, Inc., 145 South Miami Ave., Village of Cleves, Ohio, 45002, (800-543-7412)].
- 8.1.2 At least two Model PS-1 sample cartridges and filters assembled for PS-1 sampler.
- 8.1.3 GMW Model PS-I calibrator and associated equipment General Metal Works, Inc., Model **GMW-40**, 145 South Miami Ave., Village of Cleves, Ohio, 45002, (800-543-7412).
- 8.1.4 Ice chest to store samples at O-C after collection.
- 8.1.5 **Data** sheets for each sample for recording the location and sample time, duration -of sample, starting time, and volume of air **sampled**.
- 8.1.6 Airtight, labeled **screw-capped** container sample **cartridges** (wide mouth, preferably glass with Teflon **seal** or other **noncontaminating** seals) to hold filter and adsorbent **cartridge** during **transport** to analytical laboratory.
- 8.1.7 Portable Tripod Sampler (optional) - user prepared (38).
- 8.2 Sample Clean-up and Concentration
- 8.2.1 Soxhlet extractors capable of extracting GMW Model PS-1 filter and adsorbent cartridges (2.3" x 5" length), 500 mL flask, and condenser.

- 8.2.2 Pyrex glass tube furnace system for activating silica gel at 180-C under **purified** nitrogen gas purge for an hour, with capability of raising temperature **gradually**.
- 8.2.3 Glass vial, 40 **mL**.
- 8.2.4 **Erlenmeyer** flask, 50 **mL** - best source.

Note: Reuse of glassware should **be** minimized to avoid the risk of cross contamination. All glassware **that** is used, **especially** glassware that is reused, must be scrupulously cleaned as **soon** as possible after use. Rinse glassware with the last solvent used in it and then with high-purity acetone and hexane. Wash With hot water containing detergent. Rinse with copious amount of tap water and several portions of distilled water. Drain, dry, and heat a muffle **furnace** at 400-C for 2 to 4 hours. Volumetric glassware must not be heated in a muffle furnace; rather, it should be rinsed with high-purity acetone and hexane. After the glassware is dry and cool, rinse it with hexane, and store it inverted or capped with solvent **rinsed aluminum** foil in a clean environment.

- 8.2.5 Polyester gloves for handling cartridges and **filters**.
- 8.2.6 Minivials - 2 **mL**, **borosilicate** glass, with conical reservoir and screw caps lined with Teflon-faced silicone disks, and a vial holder.
- 8.2.7 Stainless steel **Teflon9(R)** coated spatulas and spoons.
- 8.2.8 Kuderna-Danish (**KD**) apparatus - 500 **mL** evaporation flask (Kontes K-570001-500 or equivalent), 10 **mL** graduated concentrator tubes (Kontes K-570050-1025 or equivalent) with ground-glass stoppers, and **3-ball** macro Snyder Column (Kontes K-5700010500, K-50300-0121, and K-569001-219, or equivalent).
- 8.2.9 Adsorption columns for column chromatography - 1 cm x 10 cm with stands.
- 8.2.10 Glove box for working with extremely toxic standards and reagents with explosion-proof hood for venting fumes from solvents, reagents, etc.
- 8.2.11 Vacuum Oven - Vacuum drying oven system capable of maintaining a vacuum at 240 torr (flushed with **nitrogen**) overnight.
- 8.2.12 Concentrator tubes and a nitrogen evaporation apparatus with variable flow rate - best source.
- 8.2.13 Laboratory refrigerator with chambers operating at 0-C and 4-C.
- 8.2.14 Boiling chips - solvent extracted, **10/40** mesh silicon carbide or equivalent.
- 8.2.15 Water bath - heated, with concentric ring cover, capable of temperature control (+/-5-C).
- 8.2.16 Vortex evaporator (optional).

## 8.3 Sample Analysis

### 8.3.1 Gas Chromatography with Flame Ionization Detection (**FID**).

**8.3.1.1** Gas chromatography: Analytical system complete with gas chromatography suitable for on-column injections and all required **accessories**, including detectors, column supplies, recorder, gases, **and syringes**. A data system for measuring peak **areas** and/or **peak** heights is recommended.

**8.3.1.2** Packed Column: 1.8-m x 2-mm I.D. glass **column** packed with 3% OV-17 on Chromosorb W-AW-DMCS (**100/120** mesh) or equivalent (Supelco Inc., Supelco Park, **Bellefonte**, Pa. Supelco **SPB-5**).

**8.3.1.3** Capillary Column: 30-m x **0.25-mm** ID fused **silica** column coated with 0.25  $\mu$  thickness 5 % phenyl, 90 % methyl **siloxane** (Supelco Inc., Supelco Park, Bellefonte, Pa).

**8.3.1.4** **Detector**: Flame Ionization (**FI**).

### 8.3.2 Gas **Chromatograph** with **Mass** Spectroscopy Detection Coupled with Data Processing System (**GC/MS/DS**).

**8.3.2.1** The GC must be equipped for temperature programming, and all required accessories must be available, including **syringes**, gases, and a capillary column. The GC injection port must be designed for capillary columns. The use of splitless injection techniques is recommended. On-column injection techniques can be used but they may severely reduce column lifetime for nonchemically bonded columns. In this protocol, a 1-3  **$\mu$ L** injection volume is used consistently. With some GC injection ports, however, 1  **$\mu$ L** injections may produce some improvement in precision and **chromatographic** separation. A 1  **$\mu$ L** injection volume may be used if adequate sensitivity and precision can be achieved.

NOTE: If 1  **$\mu$ L** is used as the injection volume, the injection volumes for all extracts, blanks, calibration solutions and performance check samples must be 1  **$\mu$ L**.

**8.3.2.2** Gas **Chromatograph-Mass** Spectrometer Interface. The gas **chromatograph** is usually coupled directly to the mass spectrometer source. The interface may include a diverter valve for shunting the column effluent and isolating the mass spectrometer source. All components of the interface should be glass **or** glass-lined stainless steel. The interface components should be compatible with 320-C temperatures. Cold spots and/or active surfaces (adsorption sites) in the **GC/MS** interface can cause **peak** tail 1 **ng** and peak broadening. It is recommended that the GC column be **fitted directly** into the MS source. Graphitic ferrules should be avoided in the GC injection area since they may adsorb **PAHs**. **Vespel(R)** or equivalent **ferrules** are recommended.

- 8.3.2.3 Mass Spectrometer. The static resolution of the instrument must be maintained at a minimum of 10,000 (10 percent valley). The mass spectrometer should be operated in the selected ion mode (**SIM**) with a total cycle time (including voltage reset time) of one second or less (Section 14.2).
- 8.3.2.4 Mass Spectrometer. Capable of **scanning** from 35 to **500 amu** every 1 **sec** or less, using 70 volts (nominal) electron energy in the **electron** impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for **decafluorotriphenylphosphine (DFTPP)** which **meets** all of the criteria (Section 14.5-1).
- 8.3.2.5 Data System. A dedicated computer **data** system is employed to control the **rapid** multiple ion monitoring process and to acquire the data. Quantification data (**peak** areas or peak heights) and multi-ion detector (MID) traces (displays of intensities of each m/z being monitored as a function of time) must be acquired during the analyses. **Quantifications** may be reported based upon computer-generated **peak areas** or upon measured **peak** heights (chart recording). The detector zero setting must allow peak-to-peak measurement of the noise on the base line.
- 8.3.2.6 GC Column. A fused **silica** column (50-m x **0.25-mm** I.D.) HP Ultra #2 **crosslinked** 5% phenyl methylsilicone, 0.25  $\mu$ m **film thickness** (Hewlett-Packard Co., Crystal Lake, IL) is utilized to separate individual **PAHs**. Other columns may be used for determination of **PAHs**. Minimum acceptance criteria must **be determined** as per Section 14.2. At the beginning of each 12-hour period (after mass resolution has been demonstrated) during which sample extracts or concentration calibration solutions will be analyzed, column operating conditions must be attained for the required separation on the column to be used for samples.
- 8.3.2.7 Balance - Mettler balance or equivalent.
- 8.3.2.8 **All** required syringes, gases, and other pertinent supplies **to** operate the **GC/MS** system.
- 8.3.2.9 Pipettes, micropipettes, syringes, **burets**, etc., to make calibration and spiking solutions, dilute samples if necessary, etc., including syringes for accurately measuring volumes such as 25  **$\mu$ L** and 100  **$\mu$ L**.
- 8.3.3 High Performance Liquid Chromatography (**HPLC**) System.
- 8.3.3.1 Gradient **HPLC** system - Consisting of **acetonitrile** and water phase **reservoirs**; mixing **chamber**; a high pressure pump; an injection valve (automatic sampler with an optional 25  **$\mu$ L loop** injector); a Vydac C-18 bonded phase reverse phase (**R**) column, (The **Separations** Group, P.O. Box 867, Hesperia, CA 92345) or equivalent (**25-cm** x **4.6-mm** ID); a variable wavelength W/Fluorescence detector and a data system or strip chart recorder. A **Spectra** Physics 8100 liquid **chromatograph** multi-microprocessor controlled, with ternary gradient pumping system, constant flow, autosampler injector (10  **$\mu$ L** injection loop), and column oven (optional) .

- 8.3.3.2 Guard column - **5-cm** guard column pack with Vydac reverse phase C-1 8 material.
- 8.3.3.3 Reverse phase analytical column - Vydac or equivalent, C-18 bonded phase R column (The Separation Group, P. O. Box 867, **Hesperia, Ca., 92345**), **4.6-mm x 25-cm, 5-micron** particle diameter.
- 8.3.3.4 **LS-4** fluorescence spectrometer, **Perkin Elmer**, separate excitation and emission, monochromator positioned by **separate microprocessor-controlled** flow cell and wave length **programming** ability (optional).
- 8.3.3.5 **Ultraviolet/visible** detector, Spectra Physics **8440**, deuterium **Lamp**, capable of programmable wavelengths (optional),
- 8.3.3.6 Dual channel Spectra Physics 4200 Computing Integrator, measures peak **areas** and retention times from recorded **Chromatographs**. IBM PC XT will Spectra Physics **Labnet** system for data collection and storage (optional).

## 9.0 Reagents and Materials

### 9.1 Sample Collection

- 9.1.1 Acid-washed **quartz** fiber filter - 105 mm micro quartz fiber binderless **filter** (General **Metal** Works, Inc., Cat. No. GMW **QMA-4**, 145 South Miami Ave., Village of Cleves, Ohio, 45002 [**800-543-7412**] or Supelco Inc., Cat. No. 1-62, Supelco Park, Bellefonte, PA, 16823-0048).
- 9.1.2 Polyurethane foam (**PUF**) - 3 inch thick sheet stock, olyether type (**density 0.022 g/cm3**) used in furniture upholstery (General Metal Works, Inc., Cat. No. PS-1-16, 145 South Miami Ave., Village of Cleves, Ohio, **45002 [800543-7412]** or Supelco Inc., Cat. No. 1-63, Supelco Park, Bellefonte, PA **16823-0048**).
- 9.1.3 XAD-2 resin - Supelco Inc., Cat. No. 2-02-79, Supelco Park, Bellefonte, PA, **16823-0048**.
- 9.1.4 Hexane-rinsed aluminum foil - best source.
- 9.1.5 Hexane-reagent grade, best source.

### 9.2 Sample Clean-up and Concentration

#### 9.2.1 **Soxhlet** Extraction

- 9.2.1.1 Methylene **chloride** - chromatographic grade, **glass-di** stilled, best source.
- 9.2.1.2 Sodium **sulfate**, anhydrous - (ACS) granular anhydrous (**purified** by washing with methylene chloride followed by heating at 400-C for 4 **hrs** in a shallow **tray**).
- 9.2.1.3 Boiling chips - solvent extracted, approximately **10/40** mesh (silicon carbide or equivalent).
- 9.2.1.4 Nitrogen - high purity grade, best source.
- 9.2.1.5 Ether - chromatographic grade **glass-distilled**, best source.

- 9.2.1.6 Hexane - chromatographic grade, glass-distilled, best source.
- 9.2.1.7 Dibromobiphenyl - chromatographic grade, best source. Used for internal standard.
- 9.2.1.8 **Decafluorobiphenyl** - chromatographic grade, best source. Used for internal standard.

## 9.2.2 Solvent Exchange

- 9.2.2.1 Cyclohexane-chromatographic grade, glass-distilled, best source.

## 9.2.3 Column Clean-up

### Method 610

- 9.2.3.1 Silica gel - high purity grade, type 60, 70-230 mesh; extracted in a Soxhlet apparatus with methylene chloride for 6 hours (minimum of 3 cycles per hour) and activated by **heating in** a foil-covered glass container for 24 hours at 130-C.
- 9.2.3.2 Sodium sulfate, anhydrous - (ACS) granular anhydrous (See Section 9.2.1.2).
- 9.2.3.3 Pentane - chromatographic grade, glass-distilled, best source.

### Lobar Prepacked Column

- 9.2.3.4 Silica gel **lobar prepacked** column - E. Merck, **Darmstadt**, Germany Size **A(240-10) Lichroprep Si** (40-63 urn)].
- 9.2.3.5 Precolumn containing sodium sulfate - American Chemical Society (ACS) **granular** anhydrous (**purified** by washing with methylene chloride followed by heating at 400-C for 4 hours in a shallow tray).
- 9.2.3.6 **Hexane-chromatographic grade**, glass-distilled, best source.
- 9.2.3.7 Methylene chloride - chromatographic grade, glass distilled, best source.
- 9.2.3.8 Methanol - **chromatographic grade**, glass-distilled, best source.

## 9.3 Sample Analysis

### 9.3.1 Gas Chromatography Detection

- 9.3.1.1 Gas cylinders of hydrogen and helium - ultra high purity, best source.
- 9.3.1.2 Combustion air - **ultra high** purity, best source.
- 9.3.1.3 Zero air - Zero air may **be** obtained from a cylinder or **zero-grade** compressed air scrubbed with **Drierite(R)** or silica gel and **5A** molecular sieve or activated charcoal, or by catalytic cleanup of ambient air. All zero air should be passed through a liquid argon cold trap for final cleanup.

9.3.1.4 Chromatographic-grade stainless steel tubing and stainless steel plumbing fittings - for interconnections. [Alltech Applied Science, 2051 Waukegan Road, Deerfield, IL, 60015, (312) 948-8600].

Note: All Such materials in contact with the sample, analyte, or support gases prior to analysis should be stainless steel or other inert metal. Do not use plastic or Teflon(R) tubing or fittings.

9.3.1.5 Native and isotopically labeled PAHs isomers for calibration and spiking standards - [Cambridge Isotopes, 20 Commerce Way, Woburn, MA, 01801 (617547-1818)]. Suggested isotopically labeled PAH isomers are:

- o perylene - d12
- o chrysene - d12
- o acenaphthene - d10
- o naphthalene - d8
- o phenanthrene - d10

9.3.1.6 Decafluorotriphenylphosphine (DFTPP) - best source, used for tuning GUMS.

9.3.2 High Performance Liquid Chromatography Detection

9.3.2.1 Acetonitrile - chromatographic grade, glass-distilled, best source.

9.3.2.2 Boiling chips - solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

9.3.2.3 Water - HPLC Grade. Water must not have an interference that is observed at the minimum detectable limit (MDL) of each parameter of interest.

9.3.2.4 Decafluorobiphenyl - HPLC grade, best source (used for internal standard).

10.0 Preparation of Sample Filter and Adsorbent

10.1 Sampling Head Configuration

10.1.1 The sampling head (Figure 2) consist of a filter holder compartment followed by a glass cartridge for retaining the adsorbent.

10.1.2 Before field use, both the filter and adsorbent must be cleaned to <math>c10</math> ng/apparatus of B[a]P or other PAHs.

10.2 Glass Fiber Filter Preparation

10.2.1 The glass fiber filters are baked at 600-C for five hours before use. To ensure acceptable filters, they are extracted with methylene chloride in a Soxhlet apparatus, similar to the cleaning of the XAD-2 resin (see Section 10.3):

- 10.2.2 The extract is concentrated and analyzed by either GC or HPLC. A filter blank of < 10 ng/filter of B[a]P or other **PAHs** is considered acceptable for field use.

### 10.3 XAD-2 Adsorbent Preparation

- 10.3.1 For initial cleanup of the XAD-2, a batch of XAD-2 (approximately 60 **grams**) is placed in a Soxhlet apparatus [see Figure 3(a)] and extracted with methylene chloride for 16 hours at approximately 4 cycles per hour.
- 10.3.2 At the end of the initial Soxhlet **extraction**, the spent methylene chloride is discarded and replaced with fresh reagent. The XAD-2 resin is once again extracted for 16 hours at approximately 4 cycles per hour.
- 10.3.3 The XAD-2 resin is removed from the Soxhlet apparatus, places **in** a vacuum oven connected to an ultra-purge nitrogen gas stream and dries at room temperature for approximately **2-4** hours (until no solvent odor is detected).
- 10.3.4 A nickel screen (mesh size **200/200**) is fitted to the bottom of a hexane-rinsed glass cartridge to retain the XAD-2 resin.
- 10.3.5 The Soxhlet extracted/vacuum dried XAD-2 resin is placed into the sampling car&ridge (using polyester gloves) to a depth of approximately 2 inches. This should require approximately 55 grams of adsorbent.
- 10.3.6 The glass module containing the XAD-2 adsorbent is wrapped with hexane-rinsed aluminum foil, placed in a labeled container and tightly sealed with Teflon(R) tape.
- 10.3.7 At least one assemble. cartridge from each batch must **be** analyzed, as a laboratory blank,-using the procedures described in Section 13, before the batch is considered acceptable for field use. A blank of c10 ng/cartridge of **B[a]P** on other **PNA's** is considered acceptable.

### 10.4 PUF Sampling Cartridge Preparation

- 10.4.1 The PUF adsorbent is a **polyether-type** polyurethane foam (density No. 3014 or 0.0225 **g/cm3**) used for furniture upholstery.
- 10.4.2 The PUF inserts are **6.0-cm** diameter **cylindrical** plugs cut from **3-inch** sheet stock and should fit, with slight compression, in the glass cartridge, supported by the wire screen (see Figure 1). During cutting, the die is rotated at high speed (e.g., in a drill press) and continuously lubricated with water.
- 10.4.3 For initial cleanup, the **PUF** plug is placed in a Soxhlet **apparatus** [see Figure **3(a)**] and extracted with acetone for **14-24** hours at approximately 4 cycles per hour.

Note: When cartridges are re-used, 5 % diethyl ether in n-hexane can be used as the cleanup solvent.

- 10.4.4 The extracted PUF is placed in a vacuum oven connected to a water aspirator and dried at room **temperature** for approximately 2-4 hours (until no solvent odor is **detected**).
- 10.4.5 The PUF is placed into the glass sampling cartridge using polyester gloves. The module is wrapped with hexane-rinsed aluminum foil, placed in a labeled container, and tightly sealed.
- 10.4.6 At **least** one assembled cartridge from each batch must **be** analyzed, as a laboratory blank, using the procedures **described** in Section 13, before the batch is considered acceptable for field use. A blank level of c10 **ng/plug** for single compounds is considered to be acceptable.

## 11.0 Sample Collection

### 11.1 Description of Sampling Apparatus

- 11.1.1 The entire sampling system **can** be a **modification** of a traditional high volume sampler (see **Figure 4**) or a portable sampler (see Figure 5). A unit **specifically** designed for this method is commercially available (Model PS-1 General Metal Works, Inc., **Village** of Cleves, Ohio).
- 11.1.2 The sampling module consists of a glass **sampling** cartridge and an air-tight metal cartridge holder, as outlined in Section 10.1. The adsorbent (**XAD-2** or **PUF**) is retained in the glass **sampling** cartridge.

### 11.2 Calibration of Sampling System

Each sampler is to be calibrated: 1) when new; 2) after major repairs or maintenance; 3) whenever any audit point deviates from the calibration curve by more than 7 %; 4) when a different sample collection media, other than that which the sampler was originally calibrated to, will be used for sampling; or 5) at the frequency **specified** in the user Standard Operating Procedure (SOP) manual in which **the** samplers are **utilized**.

#### 11.2.1 Calibration of Flow Rate Transfer Standard

**Calibration** of the modified high volume air sampler in the field is performed using a calibrated **orifice flow** rate transfer standard. The flow rate transfer standard **must** be certified in the laboratory against a positive displacement **rootsmeter** (see Figure 6). Once **certified**, the **recertification** is performed rather infrequently if the **orifice** is protected from damage. Recertification of the orifice flow rate transfer standard is performed once per year utilizing a set of five (5) multihole resistance plates.

Note: The 5 multihole resistance plates are used to change the flow through the orifice so that several points can be obtained for the **orifice calibration curve**.

- 11.2.1.1 Record the room temperature (tl in -C) and barometric pressure (**Pb** in mm Hg) on Orifice Calibration Data Sheet (see Figure 7). Calculate the room **temperature** in **-K** (absolute temperature) and record on **Orifice Calibration Data Sheet**.

$$tl \text{ in } \mathbf{K} = 273 + tl \text{ in } \mathbf{-C}$$

- 11.2.1.2 Set up laboratory **orifice** calibration equipment as illustrated in Figure 6. Check the oil level of the rootsmeter prior to starting. There are three oil level indicators, one at the clear plastic end, and two sight glasses, one at each end of the measuring chamber.
- 11.2.1.3 Check for leaks by clamping both manometer lines blocking the **orifice** with cellophane tape, turning on the high volume motor, and noting any change in the rootsmeter's **reading**. If the rootsmeter's reading changes, then there is a **leak** in the system or in the tape. Eliminate the leak before proceeding. If the rootsmeter's reading remains constant, turn off the **hi-vol** motor, remove the cellophane tape, and unclamp both manometer lines.
- 11.2.1.4 Install the **5-hole** resistance plate between the **orifice** and the **filter** adapter.
- 11.2.1.5 Turn manometer tubing connectors one turn counterclockwise. Make sure all **connectors** are **open**.
- 11.2.1.6 Adjust both manometer midpoints by sliding their movable scales until the zero point corresponds with the bottom of the meniscus. Gently shake or tap to remove any air bubbles and/or liquid remaining on tubing connectors. (If additional liquid is **required** for the water manometer, remove tubing connector and add clean water).
- 11.2.1.7 Turn on the **hi-vol** motor and let it run for **five** minutes to set the motor brushes.
- 11.2.1.8 Record both manometer readings-orifice water manometer (**H**) and **rootsmeter** mercury manometer (I?). (Note: H is the sum of the difference from zero (0) of the two column heights.)
- 11.2.1.9 Record the time, in minutes, required to pass a known volume of air (approximately **200-300 ft<sup>3</sup>** of air for each resistance plate) through the **rootsmeter** by using the rootsmeter's digital volume dial and a stopwatch.
- 11.2.1.10 Turn off the high volume motor.
- 11.2.1.11 Replace the **5-hole** resistance plate with the **7 hole** resistance plate.
- 11.2.1.12 **Repeat** Sections 11.2.1.3 through 11.2.1.10.
- 11.2.1.13 Repeat for each resistance plate. Note results on Orifice Calibration Data Sheet (see Figure 7). Only a minute is needed for warm-up of the motor. Be sure to tighten the **orifice** enough to eliminate any leaks. Also check the gaskets for cracks.

Note: The placement of the orifice prior to the rootsmeter causes the pressure at the inlet of the rootsmeter to be reduced below atmospheric conditions, thus causing the measured volume to be incorrect. The volume measured by the rootsmeter must be corrected.

11.2.1.14 Correct the measured volumes with the following formula and record the standard volume on the **Orifice** Calibration Data Sheet:

$$V(\text{std}) = V(\text{m}) \frac{P1 - \Delta P}{P(\text{std})} \frac{T1}{T(\text{std})}$$

where:

- V(std)** = standard volume (std m<sup>3</sup>).
- V(m)** = actual volume measured by **the rootsmeter** (m<sup>3</sup>).
- P1** = barometric pressure during calibration (mm Hg).
- Δ P** = differential pressure at inlet to volume meter (mm Hg).
- P(std)** = 760 mm **Hg**.
- T(std)** = 298 **K**.
- T1** = ambient temperature during calibration (**K**).

11.2.1.15 Record standard volume on Orifice Calibration Data Sheet.

11.2.1.16 The standard flow rate as measured by the rootsmeter can now be calculated using the following formula:

$$Q(\text{std}) = \frac{V(\text{std})}{@}$$

where:

**Q(std)** = standard volumetric-flow rate, std **m<sup>3</sup>/min.** = elapsed time, min.

11.2.1.17 Record the standard flow rates to the **nearest** 0.01 std **m<sup>3</sup>/min.**

11.2.1.18 Calculate and record  $(\Delta H(P1/P(\text{std})) * (298/T1))^{0.5}$  value for each standard flow **rate**.

11.2.1.19 Plot **each**  $(\Delta H(P1/P(\text{std})) * (298/T1))^{0.5}$  value (y-axis) versus its associated standard flow **me** (x-axis) on arithmetic graph paper, **draw** a line of best fit between the individual plotted points and calculate the linear regression slope (**M**) and intercept (**b**).

11.2.1.20 Commercially available calibrator kits are available [General Metal Works Inc., Model **GMW-40**, 145 South Miami Avenue, Village of Cleves, Ohio, 45002 (1-800-543-7412)].

- 11.2.2 Calibration of The High Volume Sampling System Utilizing Calibrated Multi-point Flow Bate Transfer Standard.
- 11.2.2.1 **The airflow** through the sampling system can be monitored by a **venturi/magnehelic** assembly, as illustrated in Figure 4 or by a u-tube assembly connected to **the** high volume portable design as illustrated in Figure 5. The field sampling system must **be** audited every six months using a flow rate **transfer** standard, as described in the U.S. EPA High Volume Sampling Method, 40 CFR 50, Appendix **B**. A single-point calibration must be performed before and after each sample **collection**, using a transfer standard calibrated as described in Section 11.2.1.
- 11.2.2.2 Prior to initial multi-point calibration, a “dummy” adsorbent cartridge and **filter** are placed in the sampling head and the sampling motor is activated. The flow control valve is fully opened and the voltage variator is adjusted so that a sample flow rate corresponding to 110 % of the desired flow rate (typically 0.20 - 0.28 **m<sup>3</sup>/min**) is indicated on **the Magnehelic** gauge (based on the previously obtained multi-point calibration curve). The motor is allowed to **warm** up for 10 minutes and then the flow control valve is adjusted to achieve the desired flow rate. Turn off the sampler. The ambient temperature and barometric pressure should be recorded on the Field Calibration Data Sheet (Figure 9).
- 11.2.2.3 The flow rate transfer standard is placed on the sampling head, and a manometer is connected to the tap on the transfer standard **using** a length of tubing. **Properly** align **the** retaining rings with filter holder and secure by tightening the three screw clamps. Set the zero level of **the** manometer. Attach the magnehelic gage to the sampler venturi quick release connections. Adjust the zero (if needed) using the zero adjust screw on the face of the gage.
- 11.2.2.4 Turn the flow control valve to the fully open position and turn the sampler on. Adjust the flow control valve until a magnehelic reading of approximately 70 in is obtained. Allow the magnehelic and manometer readings to stabilize and record these values.
- 11.2.2.5 Adjust the flow control valve and **repeat** until six or seven **uniformly** spaced magnehelic readings are recorded spanning the **range** of approximately 40-70 in. **Record** the **readings** on the Field Calibration Data Sheet (see Figure 9).

Note: Use of some **filter/sorbent** media combinations may restrict the airflow resulting in a maximum magnehelic reading of 60 in. or less. In such cases, a variable transformer should be placed in-line between the 110 volt power source and the sampler so that the line voltage **can** be increased **sufficiently** to obtain a maximum magnehelic reading approaching 70 in.

11.2.2.6 Adjust the orifice manometer reading for **standard** temperature and pressure using the following equation:

$$X = (\text{delta H } (P(a)/P(\text{std})) T(\text{std})/T(a)) 0.5$$

where:

x = adjusted manometer **reading** to standard temperature, and pressure (in water).  
 delta H = **observed** manometer reading (in water).  
 P(a) = current barometric pressure (mm Hg).  
 P(std) = 760 mm Hg.  
 T(a) = **current** temperature (**K**), (**K** = -**C** + 273).  
 T(std) = standard **temperature** (298 K).

11.2.2.7 Calculate the standard flow rate for each **corrected** manometer reading by the following equation:

$$Q(\text{std}) = \frac{x - b}{M}$$

where:

Q(std) = standard flow late (**m3/min**).  
 M = slope of flow rate transfer standard calibration **curve**.  
 x = corrected manometer reading from 11.2.2.6 (in water).  
 b = intercept of flow rate transfer standard calibration curve.

11.2.2.8 Adjust the magnehelic gage readings to standard temperature and pressure using the following equation:

$$M(\text{std}) = \frac{(M)P(a) T(\text{std})}{P(\text{std}) T(a)} * 0.5$$

where:

M(std) = adjusted **magnehelic-reading** to standard **temperature** and pressure (inches of water).  
 M = **observed** magnehelic reading (inches of water).  
 P(a) = ambient atmospheric pressure (mm Hg).  
 P(std) = standard pressure (760 mm Hg).  
 T(a) = ambient temperature (**K**), (**K** = -**C** + 273).  
 T(std) = standard temperature (298 K).

- 11.2.2.9 Plot each Mstd value (y-axis) versus its associated Qstd standard (x-axis) on arithmetic graph paper. Draw a line of best fit between the individual plotted points. This is the calibration **curve** for the venturi. Retain with sampler.
- 11.2.2.10 Record the corresponding Qstd for each Mstd under Qstd column on Field Calibration Data Sheet, **Figure 9**.
- 11.2.3 Single-point Audit of The High Volume Sampling System Utilizing Calibrated Flow Rate Transfer Standard.
- 11.2.3.1 A single point flow audit check is performed before and after each sampling period utilizing the Calibration Flow Rate Transfer Standard (Section 11.2.1).
- 11.2.3.2 Prior to single point audit, a “dummy” adsorbent cartridge and **filter** are placed in the sampling head and the sampling motor is activated. The flow control valve is fully opened and the voltage variator is adjusted so that a sample flow **rate** corresponding to 110% -of the desired flow rate (typically 0.20-0.28 **m<sup>3</sup>/min**) is indicated on the magnehelic gauge (based on the previously obtained multi-point calibration curve). The motor is allowed to **warm** up for 5 minutes and then the flow control valve is adjusted to achieve the desired flow rate. Turn off the sampler. The ambient temperature and barometric pressure should be recorded on a Field Test Data Sheet (Figure 10).
- 11.2.3.3 The flow rate transfer standard is placed on the sampling head.
- 11.2.3.4 Properly align the retaining rings with **filter** holder and secure by tightening the three screw clamps.
- 11.2.3.5 Using tubing, attach one manometer connector to the pressure tap of the transfer standard. Leave the other connector open to the atmosphere.
- 11.2.3.6 Adjust the manometer midpoint by sliding the movable scale until the zero point corresponds with the water meniscus. Gently shake or tap to remove any **air** bubbles and/or liquid remaining on tubing connectors. (If additional liquid is required, remove tubing connector and add clean water.)
- 11.2.3.7 Turn on high volume motor and let run for 5 minutes.
- 11.2.3.8 Record the pressure differential indicated, delta H, in inches of water. Be sure stable delta H has been established.
- 11.2.3.9 Record the observed magnehelic gauge **reading**, in inches of water. Be sure stable M has **been** established.
- 11.2.3.10 Using previously established Flow Rate Transfer Standard curve, calculate Qstd (see steps 11.2.2.6 11.2.2.7).
- 11.2.3.11 Using previously established venturi calibration curve, calculate the indicated Qstd (Section 11.2.2.9).
- 11.2.3.12 A multi-point calibration of the Flow Rate Transfer Standard against a primary standard, must be obtained annually, as outlined in Section 11.2-1.

11.2.3.13 Remove Flow Rate Transfer Standard **and** dummy adsorbent cartridge and **filter** assembly. 11.3 Sample Collection

- 11.3.1 After the sampling system has been assembled and flow checked as described in Sections 11.1 and 11.2, it can be **used to collect** air samples, as described in Section 11.3.2.
- 11.3.2 **The** samples should **be located** in an unobstructed area, at least two meters from any obstacle to air flow. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air into the sample head.
- 11.3.3 With the empty sample module removed from the sampler, rinse all sample contact areas using reagent grade hexane in a Teflon(R) squeeze bottle. Allow the hexane to evaporate from the module before loading the samples.
- 11.3.4 Detach the lower chamber of the rinsed sampling module. While wearing disposable clean lint-free nylon or **powder free surgical** gloves, remove a clean glass **cartridge/sorbent** from its container (**wide** mouthed glass jar with a Teflon(R)-lined lid) and **unwrap** its aluminum foil covering. The foil should be replaced back in the sample container to be reused after the sample has been collected.
- 11.3.5 Insert the **cartridge** into the lower chamber and tightly reattach it to the module.
- 11.3.6 Using clean Teflon(R) tipped forceps; carefully place a clean fiber **filter** atop the **filter** holder and secure in place by clamping the filter holder ring over the filter using the three screw clamps. Insure that all module connections are tightly assembled.

Note: Failure to do so could result in air flow leaks at poorly sealed locations which could affect sample representativeness.

Ideally, sample module loading and unloading should be conducted in a controlled environment or at least a centralized sample processing **area** so that the sample handling variables **can** be minimized.

- 11.3.7 With the module removed **fran** the sampler and the flow control valve fully open, **turn** the pump on and allow it to warm-up for approximately 5 minutes.
- 11.3.8 Attach a "dummy" sampling module loaded with the exact same type of filter and **sorbent** media as that which will be used for sample collection.
- 11.3.9 With the sampler off, attach the **Magnahelic** gage to the sampler. Turn the sampler on and adjust the flow control valve to the desired flow (normally as indicated by the **cfm) magnahelic** gauge **reading** and reference by the calibration chart.

Note: Breakthrough has not been a problem for all **PAHs** outlined in Section 1.5 using this sampling method except **anthracene** and phenanthrene. Once the flow is properly adjusted, extreme care should be taken not to inadvertently alter its setting.

- 11.3.10 Turn the sampler off and remove both the “dummy” module and the Magnehelic gauge. The sampler is now **ready** for field use.
- 11.3.11 The zero reading of the sampler Magnehelic is checked. Ambient temperature, barometric pressure, elapsed time meter setting, sampler serial number, **filter** number, and adsorbent **sample** number are recorded on the Field Test Data Sheet (see Figure 10). Attach the loaded sampler module to the sampler.
- 11.3.12 The voltage variator and flow control valve are placed at the settings used in Section 11.2.2, and the power switch is turned on. The elapsed time meter is activated and the start time is recorded. The flow (Magnehelic setting) is adjusted, if necessary, using the flow control valve.
- 11.3.13 The Magnehelic reading is recorded every 6 hours during the sampling period. The calibration **curve** (Section 11.2.4) is used to calculate the flow rate. Ambient temperature, barometric pressure, and Magnehelic reading are recorded at the beginning and end of the **sampling** period.
- 11.3.14 At the end of the desired sampling period, the power is **turned** off. Carefully remove the sampling head containing the filter and adsorbent cartridge to a clean area.
- 11.3.15 While **wearing** disposable lint free nylon or surgical gloves, remove the **sorbent cartridge** from the lower module chamber and lay it on the retained aluminum foil in which the sample was originally **wrapped**.
- 11.3.16 Carefully remove the glass **fiber filter** from the upper chamber using clean Teflon(R) **tipped** forceps.
- 11.3.17 Fold the filter in half twice (sample side inward) and place it in the glass cartridge atop the sorbent.
- 11.3.18 Wrap the combined samples in aluminum foil and place them in their original glass sample container. A sample label should be completed and **affixed** to the sample container. **Chain-of-custody** should be maintained for all samples.
- 11.3.19 The glass containers should be stored in ice and protected from light to prevent possible **photo-decomposition** of collected **analytes**. If the time span between sample collection and laboratory analysis is to exceed 24 hours, sample must be kept refrigerated.

Note: Recent studies (**13,16**) have indicated that **PUF** does not retain, during storage, **B[a]P** as effectively as XAD-2. Therefore, sample holding time should not **exceed** 20 days.

- 11.3 .20 A final calculated sample flow check is performed using the calibration orifice, as **described** in Section 11.2.2. If calibration deviates by more than 10% from the initial reading, the flow **data** for that sample must be marked as suspect **and** the sampler should be inspected and/or removed from service.
- 11.3.21 At least one field **filter/adsorbent** blank will be returned to the laboratory with each group of **samples**. A field blank is treated exactly as a sample except that no air is drawn through the filter/adsorbent **cartridge** assembly.
- 11.3.22 Samples are stored at O-C in an ice chest until receipt at the analytical laboratory, after which they are refrigerated at 4-C.

## 12.0 Sample Clean-up and Concentration

Note: The following sample extraction, concentration, solvent exchange and analysis procedures are outlined for user convenience in Figure 11.

### 12.1 Sample Identification

- 12.1.1 The samples are returned in the ice chest to the laboratory in the glass sample container containing the **filter** and adsorbent.
- 12.1.2 The samples are logged in the laboratory logbook according to sample location, filter and adsorbent cartridge number **identification** and total air volume sampled (uncorrected).
- 12.1.3 If the time span between sample registration and analysis is greater than **24-hrs.**, then the samples must be kept refrigerated. Minimize exposure of samples to fluorescence light. All samples should be extracted within 1 week after sampling.

### 12.2 Soxhlet Extraction and Concentration

- 12.2.1 Assemble the Soxhlet apparatus [see Figure 3(a)]. Immediately before use, charge the Soxhlet apparatus **with** 200 to 250 **mL** of methylene chloride and **reflux** for 2 hours. Let the **apparatus** cool, disassemble it, transfer the methylene chloride to a clean glass container, and retain it as a blank for later analysis, if required. Place the adsorbent and filter together in the Soxhlet **apparatus** (the use of an extraction thimble is optional) if using XAD-2 adsorbent **in** the sampling **module**.

Note: The **filter** and adsorbent are analyzed together in order to reach detection limits, avoid questionable interpretation of the data, and minimize cost.

Since methylene chloride is not a suitable solvent for PUF, 10 ether in hexane is employed to extract the **PAHs** from the PUF resin bed separate from the methylene chloride **extraction** of the accompanying filter rather than methylene chloride for the extraction of the XAD-2 cartridge.

- 12.2.1.1 Prior to extraction, add a **surrogate** standard to the Soxhlet solvent. A **surrogate** standard (i.e., a chemically inert compound not expected to occur in an environmental sample) should **be** added to each sample, blank, and **matrix** spike sample just prior to extraction or processing. The recovery of the surrogate standard is used to monitor for unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the **measured** concentration falls within the acceptance limits. The following surrogate standards have been successfully utilized in determining matrix effects, sample process errors, etc., utilizing **GC/FID**, GUMS or HPLC analysis.

Surrogate	Concentration	Analytical Technique
<b>Dibromobiphenyl</b>	50 <b>ng/uL</b>	<b>C/FID</b>
<b>Dibromobiphenyl</b>	50 <b>ng/uL</b>	<b>GC/MS</b>
<b>Deuterated Standard</b>	50 <b>ng/uL</b>	<b>GUMS</b>
<b>Decafluorobiphenyl</b>	50 <b>ng/uL</b>	<b>HPLC</b>

Note: The **deuterated** standards will be added in Section 14.3.2. Deuterated analogs of selective **PAHs** cannot be used as surrogates for HPLC analysis due to coelution problems.

Add the surrogate standard to the Soxhlet solvent.

- 12.2.1.2 For the XAD-2 and **filter** extracted together, add 300 **mL** of methylene chloride to the apparatus and reflux for 18 hours at a rate of at least 3 cycles per hour.
- 12.2.1.3 For the PUF extraction separate from the **filter**, add 300 **mL** of 10 percent ether **in** hexane to the apparatus and reflux for 18 hours at a rate of at least 3 cycles per hour.
- 12.2.1.4 For the filter extraction, add 300 **mL** of methylene chloride to the apparatus and reflux for 18 hours at a rate of at least 3 **cYcles** per hour.

- 12.2.2 Dry the extract from the Soxhlet extraction by passing it through a drying column containing about 10 **grams** of anhydrous **sodium** sulfate. Collect the dried extract **in** a Kuderna-Danish (**K-D**) **concentrator** assembly. Wash the extractor flask and sodium sulfate column with 100 - 125 **mL** of methylene chloride to complete the quantitative transfer.
- 12.2.3 Assemble a **Kuderna-Danish** concentrator [see Figure 3(b)] by attaching a 10 **mL** concentrator tube to a 500 **mL** **evaporative** flask.

Note: Other concentration devices (vortex evaporator) or techniques may be used in place of the K-D as long **as** qualitative and quantitative recovery can be demonstrated.

- 12.2.4 Add two boiling chips, attach a three-ball macro-Snyder column to the K-D flask, and concentrate **the** extract using a water bath at 60 to 65-C. Place the K-D **apparatus** in the water bath so that the concentrator tube is about half immersed in the water and the entire rounded surface of the flask is bathed with water vapor. Adjust the **vertical** position of the apparatus and the water temperature as required to complete the concentration in one hour. At the proper **rate** of **distillation**, the balls of the column actively chatter but the chambers do not flood. When the liquid has reached an approximate volume of 5 **mL**, remove the K-D apparatus **from** the water bath and allow the solvent to drain for at **least** 5 minutes while cooling.
- 12.2.5 Remove the Snyder column and rinse the **flask** and its lower joint into the concentrator **tube** with 5 **mL** of cyclohexane.

### 12.3 Solvent Exchange

- 12.3.1 Replace the K-D apparatus equipped with a Snyder column back on the water bath.
- 12.3.2 Increase the temperature of the hot water bath to 95-100-C. Momentarily, remove the Snyder column, add a new boiling chip, and attach a two-ball micro-Snyder column. Prewet the Snyder column, using 1 **mL** of cyclohexane. **Place** the K-D **apparatus** on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the **apparatus** and the water temperature, as required, to complete concentration in **15-20** minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 **mL**, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.
- 12.3.3 When the apparatus is cool, remove the micro-Snyder column and rinse its lower joint **into** the concentrator tube with about 0.2 **mL** of cyclohexane.

Note: A 5 **mL** syringe is recommended for this operation,

Adjust the extract volume to exactly 1.0 mL with cyclohexane. Stopper the concentrator tube and store refrigerated at 4-C, if further processing will not be performed immediately. If the extract will be stored longer than 24 hours, it should be **transferred** to a Teflon(R)-sealed screw-cap vial.

## 12.4 Sample Cleanup By Solid Phase Exchange

Cleanup procedures may not be needed for relatively **clean** matrix **samples**. If the extract in Section 12.3.3 is **clear**, cleanup may not be **necessary**. If **cleanup** is not necessary, the cyclohexane extract (1 mL) can be analyzed directly by **GC/FI** detection, except the initial oven temperature begins at 30-C rather than 80-C for cleanup samples (see Section 13.3), or solvent exchange to **acetonitrile** for HPLC analysis. If cleanup is required, the procedures are presented using either **handpack** silica gel column as prescribed in Method 610 (see Section 18.0, citation No. 18 and 22) or the use of a **Lobar preppacked silica** gel column for PAH concentration and **separation**. Either approach can be employed by the user.

### 12.4.1 Method 610 Cleanup Procedure [see Figure 3(c)]

12.4.1.1 Pack a **6-inch** disposable **Pasture** pipette (10 mm I.D. x 7 cm length) with a piece of glass wool. Push the wool to the neck of the disposable pipette. Add 10 grams of activated silica gel in methylene chloride slurry to the disposable pipette. Gently tap the column to settle the silica gel and elute the methylene chloride. Add 1 **gram** of anhydrous sodium sulfate to the top of the **silica** gel column.

12.4.1.2 Prior to initial use, rinse the column with methylene chloride at 1 mL/min for 1 hr to remove any **trace** of contaminants. Preelute the column with 40 mL of pentane.

Discard the **eluate** and just prior to exposure of the sodium sulfate layer to the air, transfer the 1 mL of the cyclohexane sample extract onto the column, using an additional 2 mL of cyclohexane to complete the transfer. Allow to elute through the column.

12.4.1.3 Just prior to exposure of the **sodium** sulfate layer to the air, add 25 mL of **pentane** and continue elution of the column. Discard the pentane eluate.

Note: The pentane fraction contains the **aliphatic** hydrocarbons collected on the **filter/adsorbent** combination. If interested, this fraction may be analyzed for specific aliphatic **organics**.

Elute the column with 25 mL of methylene **chloride/pentane** (4 + 6) (V/V) and collect the eluate in a 500 mL K-D flask equipped with a 10 mL concentrator tube.

Note: This fraction contains the **B[a]P** and other moderately polar **PAHs**.

**Elution** of the column should be at a rate of about 2 **mL/min**. Concentrate the collected fraction to less than 10 **mL** by the K-D **technique**, as illustrated in Section 12.3 using pentane to rinse the walls of the glassware. The extract is now ready for HPLC or GC analysis.

Note: An additional elution through the column with 25 **mL** of methanol will collect highly polar oxygenated **PAHs** with more than one functional group. This fraction may be analyzed for **specific** polar **PAHs**. However, additional cleanup by solid phase extraction may be required to **obtain** both qualitative and quantitative data due to complexity of the **eluant**.

#### 12.4.2 Lobar Prepacked Column Procedure

12.4.2.1 The setup using the **Lobar prepacked** column consists of an injection port, septum, pump, **precolumn** containing sodium sulfate, **Lobar prepacked** column and solvent **reservoir**.

12.4.2.2 The column is cleaned and activated according to the following cleanup sequence:

Fraction	Solvent Composition	Volume (mL)
1	100% Hexane	20
2	80 % Hexane/20% Methylene Chloride	10
3	50 % Hexane/50% Methylene Chloride	10
4	100 % Methylene Chloride	10
5	95 % Methylene Chloride/5 % Methanol	10
6	80 % Methylene Chloride/20 % Methanol	10

12.4.2.3 Reverse the sequence at the end of the run and run to the 100% hexane fraction in **order** to activate the column. Discard **all** fractions.

12.4.2.4 Pre-elute the column with 40 **mL** of hexane, which is also discharged.

12.4.2.5 Inject 1 **mL** of the cyclohexane sample extract, followed by 1 **mL** injection of blank cyclohexane.

12.4.2.6 Continue elution of the column with 20 **mL** of hexane, which is **also** discharged.

12.4.2.7 Now **elute** the column with 180 **mL** of a **40/60** mixture of **methylene chloride/hexane** respectively.

12.4.2.8 Collect approximately 180 **mL** of the **40/60** methylene **chloride/hexane** mixture in a K-D concentrator assembly.

12.4.2.9 Concentrate to less than 10 **mL** with the K-D assembly as discussed in Section 12.2.

12.4.2.10 The extract is now ready for either HPLC or GC analysis.

### 13.0 Gas Chromatography Analysis with Flame Ionization Detection

13.1 Gas chromatography (GC) is a quantitative analytical technique useful for PAH **identification**. This method provides the user the flexibility of column selection (packed or capillary) and detector [flame ionization (**FI**) or mass spectrometer (MS)] selection. The mass spectrometer provides for specific identification of B(a)P; however, with system **optimization**, other **PAHs** may be qualitatively and quantitatively detected using MS (see Section 14.0). This procedure provides for common GC **separation** of the **PAHs** with subsequent detection by either **FI** or MS (see Figure 12.0). The following **PAHs** have been **quantified** by GC separation with either FI or MS detection:

Acenaphthene	Chrysene
Acenaphthylene	<b>Dibenzo(a,h)anthracene</b>
Anthracene	<b>Fluoranthene</b>
<b>Benzo(a)anthracene</b>	<b>Fluorene</b>
<b>Benzo(a)pyrene</b>	<b>Indeno(1,2,3-cd)pyrene</b>
<b>Benzo(b)fluoranthene</b>	Naphthalene
<b>Benzo(e)pyrene</b>	Phenanthrene
<b>Benzo(g,h,i)perylene</b>	<b>Pyrene</b>
<b>Benzo(k)fluoranthene</b>	

The packed column gas chromatographic method described here can not adequately resolve the following four pairs of compounds: anthracene and phenanthrene; **chrysene** and **benzo(a)anthracene**; **benzo(b)fluoranthene** and **benzo(k)fluoranthene**; and dibenzo(a,h) anthracene and **indeno(1,2,3-cd)pyrene**. The use of a **capillary** column instead of the packed column, also described in this method, should adequately resolve these **PAHs**. However, unless the purpose of the analysis can be served by reporting a quantitative sum for an unresolved PAH pair, either capillary gas chromatography/mass spectroscopy (Section 14.0) or high performance liquid chromatography (Section 15.0) should be used for these compounds. This section will address the use of **GC/FI** detection using packed or capillary columns.

13.2 To achieve maximum sensitivity with the **GC/FI method**, the extract must be concentrated to **1.0 mL**, if not already concentrated to **1 mL**. If not already concentrated to **1 mL**, add a **clean** boiling chip to the methylene chloride extract in the concentrator tube. Attach a **two-ball** micro-Snyder column. Prewet the micro-Snyder column by adding about **2.0 mL** of methylene chloride to the top. Place the micro K-D apparatus on a hot water bath (60 to 65-C) so that the concentrator tube is partially immersed in the hot water. Adjust the **vertical** position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation the balls will actively chatter but the chambers will

not flood. when the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus. Drain and cool for at least 10 minutes. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a small volume of methylene chloride. Adjust the final volume to 1.0 mL and stopper the concentrator tube.

13.3 Assemble and establish the following operating parameters for the GC equipped with an FI detector:

	<b>Capillary</b>		<b>Packed</b>
	<b>(A)</b>	<b>(B)</b>	
Identification	SPB-5 fused silica capillary, 0.25 um 5% phenyl, methyl <b>siloxane</b> bonded	SPB-5 fused silica capillary, 0.25 um 5% phenyl, methyl <b>siloxane</b> bonded	Chromosorb W-AW-DMCS (100/120 mesh) coated with 3% OV-17
Dimensions	30-m x <b>0.25-mm ID</b>	30-m x <b>0.25-mm ID</b>	1.8-m x <b>2-mm ID</b>
Carrier Gas	Helium	Helium	Nitrogen
Carrier Gas Flow Rate	28-30 <b>cm/sec</b> (1 cm/minute)	28-30 <b>cm/sec</b>	<b>30-40</b> cm/minute (1 cm/minute)
Column Program	35-C for 2 <b>min</b> ; program at <b>8-C/min</b> to 280-C and hold for 12 minutes	80-C for 2 mm; program at <b>8-C/min</b> to 280-C and hold for 12 minutes	Hold at 100-C for 4 minutes; program at <b>8-C/min</b> to 280-C and hold for 15 minutes
Detector	Flame Ionization	Flame Ionization	Flame Ionization

(A) Without column cleanup (see Section 12.4)

(B) With column cleanup (see Section 12.4.1)

13.4 Prepare and calibrate the **chromatographic** system using either the external standard technique (Section 13.4.1) or the internal standard technique (Section 13.4.2). Figure 13.0 outlines the following **sequence** involving GC calibration and retention time window determination.

13.4.1 External Standard Calibration Procedure - For each **analyte** of interest, including surrogate compounds for spiking, if used, prepare calibration standards at a minimum of five concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with methylene chloride.

Note: **All** calibration standards of interest involving selected **PAHs**, of the same concentration, can be prepared **in** the same flask.

- 13.4.1.1 Prepare stock standard solutions at a concentration of 100 **ug/uL** by dissolving 0.100 gram of assayed PAH material in methylene chloride and diluting to **volin** a 10 **mL** volumetric flask.

Note: Larger volumes **can** be used at the convenience of the analyst.

- 13.4.1.2 When compound purity is assayed to be 98 % or greater, the weight can be used without correction to calculate the concentration of the stock standard.

Note: Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent **source**.

Transfer the stock standard solutions into Teflon(R)-sealed screw-cap bottles.

- 13.4.1.3 Store at 4-C and **protect** from light- Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. **Stock** standard solutions must be replaced after 1 year, or sooner, if comparison with check standards indicates a problem.

- 13.4.1.4 **Calibration** standards at a minimum of five concentration levels should be prepared through dilution of the stock standards with methylene chloride. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC.

Note: Calibration solutions must be replaced after 6 months, or sooner, if comparison With a check standard indicates a problem.

- 13.4.1.5 Inject each calibration standard using the **technique that will** be used to introduce the actual samples into the gas **chromatograph** (e.g., 1 to 3 **uL** injections).

Note: The **same** amount must be injected each time.

- 13.4.1.6 Tabulate **peak** height or **area** responses against the mass injected. The results can **be** used to prepare a calibration curve for each **analyte**.

Note: Alternatively, for samples that are introduced into the gas **chromatograph** using a syringe, the ratio of the response to the amount injected, defined as the calibration factor (**CF**), can be calculated for each **analyte at each** standard concentration by the following equation:

$$\text{Calibration factor (CF)} = \frac{\text{Total Area of Peak}}{\text{Mass injected (in nanograms)}}$$

If the percent relative standard deviation (**%RSD**) of the calibration factor is less than 20% over the working range, linearity through the origin can be assumed, and the average calibration factor **can** be used in place of a calibration **curve**.

- 13.4.1.7 The working calibration curve or calibration factor must **be** verified on each working day by the injection of one or more calibration standards. If the response for any **analyte** varies from the predicted response by more than **+20%**, a new calibration curve must be prepared for that **analyte**. **Calculate** the **percent** variance by the following equation:

$$\text{Percent variance} = \frac{R2 - R1 \times 100}{R}$$

where:

- R2** = Calibration factor from succeeding analysis.  
**R1** = Calibration factor from **first** analysis.

- 13.4.2 Internal Standard Calibration Procedure - To use this approach, the analyst must select one or more internal standards that are similar in **analytical** behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no **internal** standard applicable to all samples can **be** suggested.

Note: It is recommended that the internal standard approach be used only when the **GC/MS** procedure is employed due to **coeluting** species.

- 13.4.2.1 Prepare **calibration** standards at a minimum of five concentration levels for each **analyte** of interest by adding volumes of one or more stock standards to a volumetric flask.
- 13.4.2.2 To each calibration standard, add a known constant amount of one or more internal standard and dilute to volume with methylene chloride.

Note: One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should **correspond** to the expected range of concentrations found in **real** samples or should define the working range of the detector.

- 13.4.2.3 Inject each calibration standard using the same introduction technique that will **be** applied to the actual samples (e.g., **1-** to **3-uL** injection).
- 13.4.2.4 Tabulate the **peak** height or **area** responses against the concentration of each compound and internal standard.
- 13.4.2.5 Calculate response factors (RF) for each compound as follows:

$$\text{Response Factor (RF)} = (\text{AsCis})/(\text{AisCs})$$

where:

- AS = **Response** for the analyte to be measured (area units or peak height).
- Ais = Response for the internal standard. (area units or peak height).
- Cis = Concentration of the internal standard, (**ug/L**).
- cs = Concentration of the analyte to be measured, (**ug/L**).

- 13.4.2.6 If the RF value over the working range is constant (**< 20% RSD**), the RF can be assumed to be invariant, and the average RF can be used for calculations.

Note: **Alternatively**, the results can **be** used to plot a calibration curve of response ratios, **AS/Ais** versus RF.

- 13.4.2.7 The working calibration curve or RF must be verified on each working day -by the measurement of one or more calibration standards.
- 13.4.2.8 If the response for any analyte **varies** from the predicted response by more than **+/-20 %**, a new calibration **curve** must be prepared for that compound.

### 13.5 Retention Time Windows **Determination**

- 13.5.1 Before analysis can be performed, the retention time windows must be established for **each** analyte,
- 13.5.2 Make sure the GC system is within optimum operating conditions.
- 13.5.3 Make three injections of the standard containing **all** compounds for retention time window determination.

Note: The retention time window must be established for each analyte throughout the course of a **72-hr** period.

- 13.5.4 The retention window is **defined** as plus or minus **three** times the standard deviation of the absolute retention times for each standard.
- 13.5.5 Calculate the standard deviation of the three absolute retention times for each single component standard. In those cases where the standard deviation for a particular standard is zero, the laboratory must substitute the standard deviation of a close **eluting**, similar compound to develop a valid retention time window.
- 13.5.6 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The **data** must **be** noted and retained in a notebook by the laboratory as part of the user SOP and as a quality assurance check of the **analytical** system.

### 13.6 Sample Analysis

- 13.6.1 Inject **1-** to **3-uL** of the **methylene** chloride extract from Section 13.2 (however, the same amount each time) using the splitless injection technique when using capillary column.

Note: Smaller (**1.0 uL**) volumes **can** be injected if automatic devices are employed\*

- 13.6.2 Record the volume injected and the resulting **peak** size in **area** units or peak height.
- 13.6.3 Using either the **internal** or **external** calibration **procedure**, determine the identity and quantity of each component **peak** in the sample chromatogram through retention time window and established calibration curve. Table 2 outlines typical retention times for selected **PAHs**, using both the packed and capillary column technique coupled with FI detection, while Figure 14.0 illustrates typical chromatogram for a packed column analysis.
- 13.6.3-1 If the **responses** exceed the linear range of the system, dilute the extract and **reanalyze**. It is recommended that **extracts** be diluted so that **all** peaks are on scale. Overlapping **peaks** are not always evident when peaks are off scale. Computer reproduction of **chromatograms**, manipulated to ensure all **peaks are** on **scale** over a **100-fold** range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak **area** integration when overlapping **peaks cause** errors in area integration.
- 13.6.3.2 Establish daily retention time windows for each analyte. Use the absolute retention time for each analyte from Section 13.5.4 as the midpoint of the window for that day. The daily retention time window equals the midpoint **+/-**three times the standard deviation determined in Section **13.5.4**.
- 13.6.3.3 Tentative identification of an analyte **occurs** when a **peak** from a sample extract falls within the daily retention **time** window.

Note: Confirmation may be required on a second GC column, or by **GC/MS** (if concentration permits) or by other **recognized** confirmation techniques if overlap of peaks occur.

13.6.3.4 Validation of GC system qualitative performance is performed through the use of the **midlevel** standards. If the mid-level standard falls outside its daily retention time window the system is out of control. Determine the cause of the problem and perform a new calibration sequence (see Section 13.4).

13.6.3.5 Additional validation of the GC system performance is determined by the surrogate standard recovery. If the recovery of the surrogate standard deviates from 100 % by not more than 20 %, then the sample extraction, concentration, clean-up and analysis is certified. If it exceeds this value, then determine the cause of the problem and correct.

13.6.4 Determine the concentration of each **analyte in** the sample according to Sections 17.1 and 17.2.1.

#### 14.0 Gas Chromatography with Mass Spectroscopy Detection

14.1 The analysis of the extracted sample for **benzo[a]pyrene** and other **PAHs** is accomplished by an electron impact gas chromatography/mass **spectrometry (EI GC/MS)** in the selected ion monitoring (**SIM**) mode with a total cycle time (including voltage reset time) of one second or less. The **GC** is equipped with an ultra No. 2 fused **silica** capillary column (50-m x **0.25-mm** I.D.) with helium carrier gas for **analyte** separation. The GC column is temperature controlled and interfaced directly to the MS ion source.

14.2 The laboratory must document that the **EI GC/MS** system is properly maintained **through** periodic **calibration** checks. The GUMS system should have the following **specifications**:

Mass range: 35-500 **amu**

Scan time: 1 **sec/scan**

GC Column: 50 m x 0.25 mm I.D. (0.25 **um film** thickness) Ultra No. 2 fused silica capillary column or equivalent

Initial column temperature and hold time: **40-C** for 4 min

Column temperature **program**: 40-270-C at **10-C/min** Final column temperature **hold**: 270-C (until **benzo[g,h,i] perylene** has eluted)

Injector temperature: 250-300-C  
Transfer **line** temperature: 250-300-C  
Source temperature: According to manufacturer's **specifications**  
Injector: **Grob-type**, splitless  
**EI** Condition: 70 eV  
Mass **Scan**: Follow manufacturer instruction for selection monitoring (**SIM**) mode.  
Sample volume: 1-3 **uL**  
**Carrier** gas: Helium at 30 **cm/sec**.

The **GC/MS** is tuned using a 50 **ng/uL** solution of **decafluorotriphenylphosphine (DFTPP)**. The **DFTPP** permits the user to tune the mass spectrometer on a daily basis. If properly tuned, the **DFTPP** key ions and ion abundance criteria should be met as outlined in Table 3.

14.3 The **GC/MS** operating conditions are **outlined** in Table 4. The **GC/MS** system can be calibrated using the external standard technique (Section 14.3.1) or the internal **standard** technique (Section 14.3.2). Figure 15.0 outlines the following sequence involving the **GC/MS calibration**.

14.3.1 External standard calibration procedure.

14.3.1.1 Prepare calibration standard of **B[a]P** or other **PAHs** at a minimum of five concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with methylene chloride. The stock standard solution of **B[a]P** (1.0 **ug/uL**) must be prepared from pure standard materials or purchased as **certified** solutions.

14.3.1.2 Place 0.0100 **grams** of native **B[a]P** or other **PAHs** on a tared aluminum weighing disk and weigh on a Mettler balance.

14.3.1.3 Quantitatively, transfer to a 10 **mL** volumetric flask. Rinse the weighing disk with several **small** portions of methylene chloride. Ensure **all** material has been transferred.

14.3.1.4 Dilute to mark **with** methylene chloride.

14.3.1.5 The **concentration** of the stock standard solution of **B[a]P** or other **PAHs** in the flask is 1.0 **ug/uL**.

Note: **Commercially** prepared **stock** standards may be used at any concentration if they are **certified** by the manufacturer or by an independent **source**.

14.3.1.6 Transfer the stock standard solutions into Teflon **sealed** screw-cap bottles. Store at 4-C **and** protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

- 14.3.1.7 Stock standard solutions must be replaced after 1 yr or sooner if **comparison** with quality control check samples indicates a problem.
- 14.3.1.8 Calibration standards at a minimum of five concentration levels should be **prepared**.

Note: One of the **calibration** standards should be at a concentration near, but above the method detection limit; the others should correspond to the range of concentrations found in the sample but should not exceed the working range of the **GC/MS** system.

Accurately pipette 1 .0 ml of the stock solution (1 **ug/uL**) into another 10 **mL** volumetric flask, dilute to mark with methylene chloride. This daughter solution contains 0.1 **ug/uL** of **B[a]P** or other **PAHs**.

- 14.3.1.9 Prepare a set of standard solutions by appropriately diluting, with methylene chloride, accurately measured volumes of the daughter **solution** (0.1 **ug/uL**).
- 14.3.1.10 Accurately pipette 100 **uL**, 300 **uL**, 500 **uL**, 700 **uL** and 1000 **uL** of the daughter solution (0.1 **ug/uL**) into each 10 **mL** volumetric flask, **respectively**. To each of these flasks, add an **internal deuterated** standard to give a **final** concentration of 40 **ng/uL** of the internal **deuterated** standard (Section 14.3.2.1). Dilute to mark with methylene chloride.
- 14.3.1.11 The concentration of **B[a]P** in each flask is 1 **ng/uL**, 3 **ng/uL**, 5 **ng/uL**, 7 **ng/uL**, and 10 **ng/uL** respectively. All standards should be stored at 4-C and protected **from** fluorescent light and should be freshly prepared once a week or sooner if **check standards** indicates a problem.
- 14.3.1.12 Analyze a constant volume (1-3 **uL**) of each calibration standard and tabulate the **area** responses of the **primary** characteristic ion of each standard **against** the mass injected. The results may be used to prepare a calibration curve for each compound. Alternatively, **if** the ratio of response to amount injected (**calibration** factor) is a constant over the working range (< 20 % relative standard deviation, RSD), **linearity** through the origin may be assumed and the average ratio or calibration factor may be used in place of a **calibration curve**.
- 14.3.1.13 The working calibration curve or calibration factor must be **verified** on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than **+/-20%**, the rest must be **repeated** using a fresh calibration standard. Alternatively, a new calibration **curve** or **calibration** factor must be prepared for that compound.

14.3.2 Internal **standard** calibration procedure.

14.3.2.1 To use this approach, the analyst must select one or more **internal** standards that are similar in analytical behavior to the compounds of interest. For analysis of **B[a]P**, the analyst should use **perylene** d12. The analyst must further demonstrate that the measurement of the **internal** standard is not affected by method or matrix interferences. The following internal standards are suggested at a concentration of 40 **ng/uL** for specific **PAHs**:

<b>Perylene - d12</b>	<b>Acenaphthene - d10</b>
<b>Benzo(a)pyrene</b>	Acenaphthene
<b>Benzo(k)fluoranthene</b>	Acenaphthylene
<b>Benzo(g,h,i)perylene</b>	<b>Fluorene</b>
<b>Dibenzo(a,h)anthracene</b>	
<b>Indeno(1,2,3-cd)pyrene</b>	Naphthalene - d8
Chrysene - d12	Naphthalene
<b>Benzo(a)anthracene</b>	<b>Phenanthrene -d10</b>
Chrysene <b>Pyrene</b>	<b>Anthracene</b>
<b>Fluoranthene</b>	
<b>Phenanthrene</b>	

- 14.3.2.2 A mixture of the above **deuterated** compounds **in** the appropriate **concentration range** are commercially available (see Section 9.3.1.5).
- 14.3.2.3 Use the base **peak** ion as the primary ion for **quantification** of the standards. If interferences **are** noted, use the next two most intense ions as the secondary ions. The internal standard is added to all calibration standards and all sample extracts analyzed by **GC/MS**. Retention time standards, column performance standards, and a mass spectrometer **tuning standard** may be included in the internal standard solution used.
- 14.3.2.4 Prepare calibration standards at a minimum of three concentration level for each parameter of interest by adding appropriate volumes of one or more stock standards to a volumetric flask. To each **calibration** standard or standard mixture, add a known constant amount of one or more of the **internal deuterated standards** to yield a resulting concentration of 40 **ng/uL** of internal standard and dilute to volume with **methylene** chloride. One of the **calibration standards** should be at a concentration near, but above, the minimum detection limit (**MDL**) and the other concentrations should **correspond** to the expected range of concentrations found in **real** samples or should **define** the working **range** of the **GC/MS** system.

- 14.3.2.5 **Analyze** constant amount (1-3 **uL**) of each **calibration** standard and tabulate the **area** of the primary characteristic ion against concentration for each compound and internal standard, and calculate the **response** factor (**RF**) for each **analyte** using the following equation:

$$RF = (AsCis)/(AisCs)$$

where:

- As** = Area of the characteristic ion for the analyte to **be** measured.  
**Ais** = Area of the characteristic ion for the internal standard.  
**Cis** = Concentration of the internal standard, (**ng/uL**).  
**cs** = Concentration of the analyte to **be** measured, (**ng/uL**).

**If** the RF value over the working **range** is a constant (< 20% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration **curve** of response ratios, **As/Ais**, vs. **RF**. Table 5. outlines key ions for selected internal **deuterated** standards.

- 14.3.2.6 The working calibration curve or **RF** must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from **the** predicted response by more than **+/-20 %**, the test must **be** repeated using a fresh calibration standard. Alternatively, a new **calibration curve** must be prepared.
- 14.3.2.7 The relative retention times for each compound in each calibration **run** should agree within 0.06 relative retention time units.

#### 14.4 Sample Analysis

- 14.4.1 It is highly recommended that the extract be screened on a **GC/FID** or **GC/PID** using the same **type** of capillary column as in the **GC/MS** procedure. This will **minimize contamination** of the GUMS system **from** unexpectedly high concentrations of organic compounds.
- 14.4.2 **Analyze** the 1 **mL** extract (see Section 13.2) by **GC/MS**. The recommended **GC/MS** operating conditions to be **used** are **specified** in Section 14.2.
- 14.4.3 If the response for any **quantitation** ion exceeds the initial **calibration** curve range of the **GC/MS** system, extract dilution must take place. Additional **internal** standard must be added to the diluted extract to maintain the required **40 ng/uL** of each internal standard in the extracted volume. The diluted **extract** must be reanalyzed.

- 14.4.4 Perform **all** qualitative and quantitative **measurements** as described in Section 14.3. The typical **characteristic** ions for selective **PAHs** are outlined in Table 6.0. Store the **extracts** at 4-C, protected from light in screw-cap **vials** equipped with unpierced Teflon(R)-lined, for future analysis.
- 14.4.5 For sample analysis, the comparison between the sample and references spectrum must illustrate:
- (1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.
  - (2) The relative intensities of the major ions should agree within **+/-20 %**. (Example: For an ion with an abundance of 50 in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70 %).
  - (3) Molecular ions present in the reference spectrum should be present **in** the sample spectrum.
  - (4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of **coeluting** compounds.
  - (5) Ions present in the **reference spectrum** but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or **coeluting peaks**. Data system library reduction **programs** can sometimes create these discrepancies.
- 14.4.6 **Determine** the concentration of each **analyte** in the sample according to Sections 17.1 and 17.2.2.

#### 14.5 GC/MS Performance Tests

- 14.5.1 Daily **DFTPP** Tuning - At the beginning of each day that analyses are to be performed, the **GC/MS** system must be checked to see that acceptable performance criteria are achieved when challenged with a 1 **uL** injection volume **containing** 50 ng of **decafluorotriphenylphosphine (DFTPP)**. The **DFTPP** key ions and ion abundance criteria that must be met are illustrated in Table 3.0. Analysis should not begin until all those criteria are met. Background subtraction should be straight **forward** and designed only to **eliminate** column bleed or instrument background ions. The **GC/MS** tuning standard should also be used to assess **GC** column performance and injection port inertness. Obtain a background correction mass spectra of **DFTPP** and check that all key ions criteria are met. **If** the criteria are not achieved, the analyst must retune the **mass** spectrometer and repeat the test until **all** criteria **are** achieved. The performance criteria must be **achieved** before any **samples**, blanks or standards are analyzed. **If any** key ion abundance **observed** for the daily **DFTPP** mass tuning check differs by more than 10% absolute

abundance from that **observed** during the previous daily tuning, the instrument must be retuned or the sample and/or calibration solution reanalyzed until the above condition is met.

- 14.5.2 Dally 1-point Initial Calibration Check - At the beginning of each work day, a daily 1-point calibration check is performed by **re-evaluating** the **midscale** calibration standard. This is the same check that is applied during the initial calibration, but one **instead** of five working standards are evaluated. Analyze the one working standards under the same conditions the initial calibration **curve** was evaluated. Analyze 1 **uL** of each of the mid-scale calibration standard and tabulate the **area** response of the primary characteristic ion against mass injected. Calculate the percent difference using the following equation:

$$\text{Difference} = \text{RF}(c) - \text{RF}(I) \cdot 100$$

**RF(I)**

Where:

**RF(I)** = average response factor from initial calibration using mid-scale standard.  
**RF(c)** = response factor from current verification check using mid-scale standard.

If the percent **difference** for the mid-scale level is greater than **10%**, the laboratory should consider this a warning limit. **If** the percent difference for the mid-scale standard is less than **20%**, the initial calibration is assumed to be valid. If the criterion is not met (**< 20 %** difference), then corrective action **MUST be** taken.

Note: Some possible problems are standard mixture **degradation**, injection port inlet contamination, contamination at the front end of the analytical **column**, and active sites in the column or **chromatographic** system. This check must be met before analysis begins. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration **MUST** be generated. This criterion **MUST** be met before sample analysis begins.

- 14.5.3 **12-hour Calibration Verification** - A calibration standard at mid-level concentration containing **B[a]P** or other **PAHs** must be performed every twelve continuous hours of analysis. Compare the standard every 12-hours with the average response factor **from** the initial calibration. If the difference for the response factor (see Section 145.2) is less than **20%**, then the **GCtMS**

system **is operative** within initial calibration values. **If** the criteria is not met (> 20% difference), then the source of the problem must be determined and a new five-point curve **MUST** be generated.

14.5.4 Surrogate Recovery - Additional validation of the **GC** system performance is determined by the surrogate standard recovery. If the **recovery** of the surrogate standard deviates from 100% by not **more** than 202, then the sample extraction, concentration, clean-up and analysis is certified. If it exceeds this value, then determine the cause of the problem and **correct**.

## 15.0 High Performance Liquid Chromatography (**HPLC**) Detection

### 15.1 Introduction

15.1.1 Detection of **B[a]P** by HPLC **has** also **been** a viable **tool** in recent years. The procedure outlined below has been written **specifically** for analysis of **B[a]P** by HPLC. However, by optimizing **chromatographic** conditions [(multiple detector fluorescence - excitation at **240 nm**, emission at **425 nm**; ultraviolet at **254 nm**)] and varying the mobile phase composition through a gradient **program**, the following **PAHs** may also be **quantitafied**:

COMPOUND	DETECTOR(1)	COMPOUND	DETECTOR(1)
Acenaphthene	W	<b>Benzo(k)fluoranthene</b>	FL
Acenaphthylene	<b>W</b>	<b>Dibenzo(a,h)anthracene</b>	FL
<b>Anthracene</b>	W	<b>Fluoranthene</b>	FL
<b>Benzo(a)anthracene</b>	<b>FL</b>	<b>Fluorene</b>	W
<b>Benzo(a)pyrene</b>	FL	<b>Indeno(1,2,3-cd)pyrene</b>	FL
<b>Benzo(b)fluoranthene</b>	F L	Naphthalene	W
<b>Benzo[e]pyrene</b>	<b>FL</b>	Phenanthrene	W
<b>Benzo(ghi)perylene</b>	FL	<b>Pyrene</b>	FL

IW = Ultraviolet

FL = Fluorescences

15.1.2 This **method** provides quantitative **identification** of the selected **PAH's** compounds listed above by high performance liquid Chromatography. It is based on **separating** of compounds of a liquid **mixture** through a liquid **chromatographic column** and **measuring** the separated components with suitable detectors.

15.1.3 The **method** involves solvent exchange, with subsequent HPLC detection involving ultraviolet (**W**) and fluorescence (FL) detection.

## 15.2 Solvent Exchange To Acetonitrile

- 15.2.1 To the extract in the concentrator tube, add 4 mL of acetonitrile and a new boiling chip; attach a **micro-snyder** column to the apparatus.
- 15.2.2 Increase **temperature** of the hot water bath to 95 to 100-C.
- 15.2.3 Concentrate the solvent as in Section 12.3.
- 15.2.4 After cooling, remove the **micro-Snyder** column and rinse its lower sections into the concentration tube with approximately 0.2 mL acetonitrile.
- 15.2.5 Adjust its volume to 1.0 mL.

## 15.3 HPLC Assembly

- 15.3.1 The HPLC system is assembled, as **illustrated** in Figure 10.
- 15.3.2 **The** HPLC system is **operated** according to the following parameters:

### HPLC Operating Parameters

Guard Column:	<b>VYDAC 201 GCCIOYT</b>
<b>Analytical</b> Column:	<b>VYDAC 201 TP5415 C-18 R (0.46 x 25 cm)</b>
Column Temperature:	27.0 +/- 2-C
Mobile Phase:	
Solvent Composition	Time (Minutes 40%)
<b>Acetonitrile/60 %</b> water	0
100% Acetonitrile	25.
100% <b>Acetonitrile</b>	35
40% <b>Acetonitrile/60 %</b> water	45

**Linear** gradient elution at 1.0 mL/min

Detector: Variable wavelength ultraviolet and fluorescence.

Flow Rate: 1.0 mL/minute

Note: To prevent irreversible absorption due to "dirty". injections and premature loss of column efficiency, a guard column is installed between the injector and the **analytical** column. The guard column is generally packed with identical material as is found **in** the **analytical** column. The guard column is generally replaced with a fresh guard column after several injections ( **50**) or when separation between compounds becomes **difficult**. The **analytical column** specified in this **procedure** has been laboratory evaluated. Other **analytical** columns may be used as long as they meet procedure and separation requirements, Table 7.0 outlines other columns uses to determine **PAHs** by HPLC.

- 15.3.3 The mobile phases are placed in separate HPLC solvent reservoirs and the pumps are set to yield a total of 1.0 **mL/minute** and **allowed** to pump for 20-30 minutes before the **first** analysis. The detectors are switched on at least 30 minutes before the first analysis. W detection at 254 **nm** is generally preferred. The fluorescence spectrometer excitation wavelengths **range** from 250 to 800 nanometers. The excitation and emission slits are both set at 10 nanometers nominal **bandpass**.
- 15.3.4 Before each analysis, the detector baseline is **checked** to ensure stable operation.

#### 15.4 HPLC Calibration

- 15.4.1 Prepare stock standard solutions at PAH concentrations of 1.00 **ug/uL** by dissolving 0.0100 **grams** of assayed material in **acetonitrile** and diluting to volume in a 10 **mL** volumetric **flask**.

Note: **Larger volumes can** be used at the convenience of the analyst. When compound purity is assayed to be 98 % or greater, the weight can be used without correction to calculate the **concentration** of the stock standard.] Commercially prepared stock standards **can** be used at any concentration if they are certified by the manufacturer or by an independent source.

- 15.4.2 Transfer the stock **standard** & ions into Teflon(R)-sealed screw-cap bottles. Store at 4-C and protect from light. St&k standards **should** be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.
- 15.4.3 Stock standard solutions must be replaced after 1 year, or sooner, if comparison with check standards indicates a problem.
- 15.4.4 Prepare calibration standards at a minimum of **five** concentration levels ranging from 1 **ng/uL** to 10 **ng/uL** by first diluting the stock standard 10:1 with acetonitrile, giving a daughter solution of 0.1 **ug/uL**. Accurately pipette 100 **uL**, 300 **uL**, 500 **uL**, 700 **uL** and 1000 **uL** of the daughter solution (0.1 **ug/uL**) into **each** 10 **mL** volumetric flask, respectively. Dilute to mark with acetonitrile. One of the concentration levels should be at a concentration near, but above, the method detection limit (**MDL**). The remaining concentration levels should correspond to the expect& range of concentrations found in real **samples** or should define the working range of the HPLC.

Note: Calibration standards must be replaced after 6 months, or sooner, if comparison with check standards indicates a problem.

- 15.4.5 Analyze **each** calibration standard (at least five levels) three times. Tabulate **area** response vs. mass injected. All calibration runs are performed as described for sample analysis in Section 15.5.1. Typical retention times for

specific **PAHs** are **illustrated in** Table 8.0. **Linear** response is indicated where a correlation coefficient of at least 0.999 for a **linear** least-squares fit of the data (concentration versus **area** response) is obtained. The retention times for each **analyte** should agree within +/- 2 %.

- 15.4.6 Once linear response has been documented, an intermediate **concentration** standard **near the** anticipated levels for each component, but at least 10 times the detection limit, should be chosen for a **daily** calibration check. The response for the various components should be within 15% day to day. If greater variability is observed, recalibration may be required or a new calibration curve must be developed from fresh standards.
- 15.4.7 The response for each component in the daily calibration standard is used to calculate a response factor according to the following equation

$$\text{RF}(c) = \frac{C(c) * V(I)}{R(c)}$$

where:

- RF(c) = response factor (usually **area** counts) for the component of interest in nanograms injected/response unit.
- C(c) = concentration (**mg/L**) of **analyte** in the daily calibration standard.
- V(I) = volume (**uL**) of calibration standard injected.
- R(C) = response (area counts) for **analyte** in the calibration standard.

## 15.5 Sample Analysis

- 15.5.1 A 100 **uL aliquot** of the sample is drawn into a clean **HPLC** injection syringe. The sample injection **loop** (10 **uL**) is loaded and an injection is made. The data system, if available, is activated **simultaneously** with the injection and the point of injection is marked on the strip and recorded.
- 15.5.2 After approximately 1 minute, the injection valve is returned to the "load" position and the syringe and valve are flushed with water **in** preparation for the next sample analysis.
- 15.5.3 After elution of the last component of interest, concentrations are calculated as described in Section 16.2.3.

Note: Table 8.0 illustrates typical retention times associated with individual **PAHs**, while Figure 17 represent a typical **chromatogram** associated with fluorescence detection.

- 15.5.4 After the last compound of interest has eluted, establish a stable baseline; the system can be now used for further sample analyses as described above.

15.5.5 If the concentration of analyte exceeds the **linear** range of the instrument, the sample should be diluted with mobile phase, or a smaller volume can be injected into the **HPLC**.

15.5.6 Calculate surrogate standard recovery on all samples, blanks and spikes. Calculate the percent difference by the following equation:

$$\% \text{ difference} = \frac{S(R) - S(I)}{S(I)} \cdot 100$$

where:

**S(I)** = surrogate injected, ng.

**S(R)** = surrogate recovered, ng.

15.5.7 Once a minimum of thirty samples of the same **matrix** have been analyzed, calculate the average percent **recovery (%R)** and standard deviation of the percent **recovery (SD)** for the surrogate.

15.5.8 For a given matrix, **calculate** the upper and lower control limit for method performance for the surrogate standard. This should be done as follows:

Upper Control Limit (**UCL**) = (**%R**) + **3(SD)**

Lower Control Limit (**LCL**) = (**%R**) - **3(SD)**

The **surrogate recovery** must fall within the control limits. If recovery is not within limits, the following is **required**:

- Check to be sure there are no **errors** in calculations surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data **and/or** reanalyze the extract if any of the above checks **reveal a problem**.
- **Re-extract** and reanalyze the **sample** if none of the above **are** a problem or flag the data as "estimated concentration."

15.5.9 Determine the concentration of each **analyte** in the **sample according to** Sections 17.1 and **17.2.3**.

## 15.6 HPLC System **Performance**

15.6.1 The **general** appearance of the **HPLC** system should be similar to that illustrated in Figure 10.

15.6.2 **HPLC** system efficiency is calculated according to the following equation:

$$N = 5.54 \frac{t(r)^2}{W^{0.5}}$$

where:

N = column efficiency (**theoretical** plates).

t(r) = retention time (seconds) of **analyte**.

W<sup>0.5</sup> = width of component **peak at** half height (seconds).

A column efficiency of **>5,000** theoretical plates should be obtained.

15.6.3 Precision of **response** for replicate HPLC injections should be +/- 10 % or less, day to **day**, for **analyte** calibration standards at 1 **ug/mL** or greater levels. At 0.5 **ug/mL** level and below, precision of replicate analyses could vary up to 25 %. Precision of retention times should be +/- 2 % on a given **day**.

15.6.4 From the calibration standards, **area** responses for each **PAH** compound can be used against the concentrations to establish working calibration curves. The calibration **curve** must be **linear** and have a correlation coefficient greater than 0.98 to be acceptable.

15.6.5 The working calibration **curve** should be checked daily with an analysis of one or more calibration standards. If the observed response (r) for any PAH varies by more than 15% from the predicted response (r), the test method must be repeated with new calibration standards. Alternately a new calibration curve must be prepared.

[Note: If  $[r(o) - r(p)]/r(p) > 15 \%$ , recalibration is necessary.]

## 15.7 HPLC Method **Modification**

15.7.1 The **HPLC** procedure has been automated by Acurex Corporation as part of their "Standard Operating **Procedure** for **Polynuclear** Aromatic **Hydrocarbon** Analysis by High Performance Liquid Chromatography Methods," as reported in Reference 9 of Section 18.

15.7.2 The system consists of a Spectra Physics 8100 Liquid **Chromatograph**, a micro-processor-controlled HPLC, a **ternary** gradient generator, and an autosampler (10 **uL** injection **loop**).

15.7.3 The **chromatographic** analysis involves an automated solvent program allowing unattended instrument operation. The solvent program consists of four timed segments using varying concentrations of **acetonitrile** in water with a constant flow rate, a constant column temperature, and a **10-minute** equilibration time, as outlined below.

#### **AUTOMATED HPLC WORKING PARAMETERS**

Solvent Time	Composition	Temperature	Pate
10 minutes equilibration T=0	40% Acetonitrile 60% Water	27.0 +/- 2-C	1 mL/min
T=25	40% Acetonitrile 60% Water		
T=35	100% <b>Acetonitrile</b>		
T=45	100g Acetonitrile 40% <b>Acetonitrile</b> 60% Water		

Table 9.0 outlines the associated **PAHs** with their minimum detection limits (**MDL**) which can be detected employing the **automated HPLC** methodology.

- 15.7.4 A **Vydac** or equivalent analytical column packed with a C18 bonded phase is used for **PAH separation** with a reverse phase guard column. The optical detection system consists of a Spectra Physics **8440 variable** Ultraviolet (**W**)/**Visible (VIS)** wavelength detector and a **Perkin Elmer LS-4** Fluorescence Spectrometer. The WMS detector, controlled by remote programmed commands, contains a Deuterium lamp with wavelength selection between 150 and 600 nanometers. It is set at 254 nanometers with the time constant (detector response) at 1.0 seconds.
- 15.7.5 The **LS-4** Fluorescence Spectrometer contains separate excitation and emission **monochromators** which are positioned by separate **microprocessor-controlled** stepper motors. It contains a Xenon discharge lamp, side-on photomultiplier and a **3-microliter** illuminated volume flow cell. It is equipped with a wavelength **programming** facility to set the monochromators automatically to a given wavelength position. This greatly enhances selectivity by changing the fluorescence excitation and emission detection wavelengths during the **chromatographic** separation in order to optimize the detection of each PAH. **The** excitation wavelengths range from 230 to 720 nanometers; the emission wavelengths range from 250 to 800 **nanometes**. The excitation and emission slits are both set at 10 nanometers nominal **bandpass**.

15.7.6 The W detector is used for detecting naphthalene, acenaphthylene and acenaphthene, and the fluorescence detector is used for the remaining **PAHs**. Table 9 outlines the detection techniques and minimum detection limit (**MDL**) employing this HPLC system. A Dual Channel Spectra Physics (**SP**) 4200 computing integrator, with a **Labnet** power supply, provides data analysis and a **chromatogram**. An IBM PC XT with a **10-megabyte** hard disk provides data storage and reporting. Both the **SP4200** and the IBM PC XT can control all functions of the instruments in the series through the **Labnet** system except for the **LS-4**, whose wavelength program is started with a **signal** from the High Performance Liquid **Chromatograph** autosampler when it injects. All data are transmitted to the XT and stored on the hard disk. Data files can later be transmitted to floppy disk storage.

## 16.0 Quality Assurance/Quality Control 16.1 General System QA/QC

- 16.1.1 Each laboratory that uses these methods is required to operate a formal **quality control program**. The minimum requirements of this **program** consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate **and** document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to **determine** if the **results** of analyses meet the performance characteristics of the method. When results of sample spikes indicate a typical **method** performance, a quality control check standard must be analyzed to **confirm** that the measurements were **performed** in an in-control mode of operation.
- 16.1.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent solvent blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is **extracted** or there is a change in reagents, a reagent solvent blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be **carried** through **all** stages of the sample preparation and measurement steps.
- 16.1.3 For each **analytical** batch (up to 20 samples), a reagent blank, matrix spike and **deuterated/surrogate** samples must be analyzed (the frequency of the spikes may be different for different monitoring programs). The blank and spiked samples must **be** tied through all stages of the sample preparation and measurement steps.
- 16.1.4 The experience of the analyst **performing** gas **chromatography** and high performance liquid chromatography is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration sample should **be** evaluated to determine if the **chromatographic** system is operating properly. Questions that should **be** asked **are**: Do the **peaks** look normal?; Is the response windows obtained comparable to the response from previous

calibrations? Careful examination of the standard **chromatogram** can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., column changed), recalibration of the system must take place.

## 16.2 Process, Field, and Solvent Blanks

- 16.2.1 **One cartridge (XAD-2 or PUF) and filter** from each batch of **approximately 20** should **be** analyzed, without shipment to the field, for the compounds of interest per to serve as a process blank. A blank level of less than 10 ng **per cartridge/filter** assembly for single **PAH** component is considered to be acceptable.
- 16.2.2 During each sampling episode, at least one cartridge and filter should be shipped to the field and returned, without drawing air through the sampler, to **serve** as a **field blank**.
- 16.2.3 During the analysis of **each** batch of samples at **least** one solvent process blank (all steps conducted but no cartridge or **filter included**) should be carried through the procedure and analyzed. Blank levels should be less than 10 **ng/sample** for single components to **be acceptable**.
- 16.2.4 **Because** the sampling **configuration (filter and backup adsorbent)** has been tested for targeted **PAHs** in the **laboratory** in relationship to collection efficiency and has been demonstrated to **be** greater than 95% for targeted **PAHs**, no field recovery evaluation **will occur** as part of the **QA/QC** program **outlined** in this section.

## 16.3 Gas **Chromatography** with Flame Ionization Detection

- 16.3.1 Under the calibration procedures (internal and external), the RSD of the calibration factor should be 20% over the linear working **range** of a five point **calibration** curve (Sections 13.4.1.6 and **13.4.2.6**).
- 16.3.2 Under the calibration procedures (internal and external), the daily working calibration curve for each **analyte** should not vary from the predicted response by more than **+/-20%** (Sections 13.4.1.7 and 13.4.2.8).
- 16.3.3 For each analyte, the retention time window must **be** established (Section **13.5.1**), verified on a daily basis (Section 13.6.3.2) and established for each **analyte** throughout the course, of a **72-hour period** (Section 13.5.3).
- 16.3.4 For each analyte, the mid-level **standard** must fall **within** the retention time window on a **daily** basis as a **qualitative** performance evaluation of the GC system (Section 13.6.3.4).
- 16.3.5 The surrogate standard recovery must not deviate from 100% by no more than **20%** (Section 13.6.3.5).

## 16.4 Gas Chromatography with Mass Spectroscopy Detection

- 16.4.1 **Section 14.5.1** requires the mass spectrometer **be** tuned daily with **DFTPP** and meet relative ion abundance requirements outlined in Table 3.
- 16.4.2 Section 14.3.1.1 requires a minimum of five **concentration** levels of each **analyte** (plus **deuterated** internal standards) be prepared to establish a calibration factor to illustrate **< 20 %** variance over the **linear** working range of the calibration **curve**.
- 16.4.3 Section 14.3.1.13 requires the **verification** of the working curve each working day (if using the external standard technique) by the measurement of one or more calibration standards. The predicted response must not vary by more than **+/-20%**.
- 16.4.4 Section 14.3.2.6 requires the initial calibration curve **be** verified each working **day** (if using the internal standard technique) by the measurement of one or more calibration standards. If the response varies by more **than** +/-20% of predicted response, a fresh **calibration curve (five point)** must be established.
- 16.4.5 Section 14.4.5 requires that for **sample** analysis, the comparison between the sample and reference spectrum illustrate:
- (1) Relative intensities of major ions in the reference spectrum (ions **> 10%** of the most abundant ion) should be present in the sample spectrum.
  - (2) The relative intensities of the major ions should agree within **+/-20 %**. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).
  - (3) Molecular ions present in the reference **spectrum** should be present in **sample** the spectrum.
  - (4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.
  - (5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or **coeluting peaks**. Data system **library** reduction programs can sometimes **create** these discrepancies.
- 16.4.6 Section 14.5.3 requires that initial calibration **curve** be verified every 12 continuous hour of analysis by **a** mid-level calibration standard. The response must be less **than** 20 difference from the initial response.
- 16.4.7 The surrogate standard recovery must not deviate from 100% by no more than 20% (Section 14.5.4).

## 16.5 High Performance Liquid Chromatography

- 16.5.1 Section 15.4.4 requires the preparation of calibration standards at a minimum of five concentration levels to establish **correlation** coefficient of at least 0,999 for a linear least-squares fit of the data.
- 16.5.2 Section 15.4.5 **requires** that the retention time for each **analyte** should agree within **+/-2%**.
- 16.5.3 A daily **calibration** check involving an intermediate standard of the initial five point **calibration curve** should be within **+/-15** from day to day.
- 16.5.4 Section 15.5.6 requires the calculation of percent difference of surrogate standard recovery in order to establish control limits:

Upper Control Limit (**UCL**) = (**%R**) + 3 (SD)

Lower Control Limit (**LCL**) = (**%R**) - 3 (SD)

The surrogate recovery must fall within the control limits.

## 17.0 Calculations

### 17.1 Sample Volume

- 17.1.1 The total **sample** volume should be corrected to standard temperature and pressure.
- 17.1.2 The total sample volume (**Vm**) is calculated from the **periodic** flow readings (**Magnehelic** readings taken in Section **11.3.13**) using the following equation.

$$Q ( m ) = \frac{Q1 + Q2 + \dots + QN}{N} * \frac{T}{1000}$$

where:

- V(m) = total sample volume (m<sup>3</sup>) at ambient conditions .
- Q1, Q2...Qn = flow rates determined at the beginning, end, and intermediate points during sampling (**m<sup>3</sup>/minute**).
- N = number of data points.
- T = elapsed sampling time (minutes).

- 17.1.3 The volume of **air** sampled can be converted to standard conditions (760 mm Hg pressure and 25-C) using the following equation:

$$V(s) = V(m) * \frac{P(A)}{7h\%} * \frac{298-}{273 + t(a)}$$

where:

V(s) = total sample volume (m<sup>3</sup>) at standard temperature and pressure (25-C and 760 mm Hg **pressure**).

V(m) = total sample flow under ambient conditions (m).

P(A) = ambient pressure (mm Hg).

t(a) = ambient **temperature** (-C) .

## 17.2 Sample Concentration

### 17.2.1 GC/FI Detection

17.2.1.1 The concentration of each analyte in the sample may be determined from the external standard technique by calculating the amount of standard injected, from the **peak** response, using the calibration curve or the calibration factor determined in Section 13.4.1.6.

17.2.1.2 The concentration of a specific analyte is calculated as follows:

$$\text{Concentration, ng/m}^3 = \frac{[(Ax)(Vt)(D)]}{[(CF)(Vi)(Vs)]}$$

where:

**CF** = calibration factor for **chromatographic** system, **peak** height or area response per mass injected, Section 13.4.1.6.

**AX**= Response for the analyte **in** the sample, **area** counts or **peak** height.

**Vt** = volume of total sample, **uL**.

**D** = Dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

**Vi** = volume of sample injected, **uL**

**vs** = total sample volume (m<sup>3</sup>) at standard temperature and pressure (25-C and 760 mm Hg), Section 17.1.3.

### 17.2.2 GC/MS Detection

17.2.2.1 When an analyte has been identified, the **quantification** of that analyte will be based on the **integrated** abundance from the monitoring of the primary characteristic ion. **Quantification** will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (see Section 14.3.2.1).

17.2.2.2 Calculate the concentration of each identified **analyte** in the sample as follows:

$$\text{Concentration; ng/m}^3 = \frac{[(A_x)(I_s)(V_t)(D)]}{[-(A_{is})(RF)(V_i)(V_s)]}$$

where:

- A<sub>x</sub>** = **area** of characteristic ion(s) for analyte being measured.  
**I<sub>s</sub>** = amount of internal **standard** injected, ng.  
**v<sub>t</sub>** = volume of total sample, **uL**.  
**D** = dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, **D = 1**, dimensionless.  
**A<sub>is</sub>** = area of characteristic ion(s) for internal standard.  
**RF** = Response factor for analyte **being measured**, Section 14.3.2.5.  
**V<sub>i</sub>** = volume of analyte injected, **uL**.  
**v<sub>s</sub>** = total sample volume (m<sup>3</sup>) at standard **temperature** and pressure (25-C and 760 mm Hg), Section 17.1.3.

### 17.2.3 HPLC Detection

17.2.3.1 The concentration of each analyte in the **sample** may be determined from the external standard technique by calculating response factor and **peak** response using the **calibration curve**.

17.2.3.2 The concentration of a specific analyte is calculated as **follows**:

$$\text{Concentration, ng/m}^3 = \frac{[(RF_c)(A_x)(V_t)(D)]}{[ (v_i) (V_s) ]}$$

where:

- RF<sub>c</sub>** = response factor (nanograms injected per **area** counts) **calculated** in Section 15.4.7.  
**A<sub>x</sub>** = response for the analyte in the sample, area counts or **peak** height.  
**v<sub>t</sub>** = volume of total sample, **uL**.  
**D** = dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, **D = 1**, dimensionless.  
**V<sub>i</sub>** = volume of sample injected, **uL**.  
**v<sub>s</sub>** = total sample volume (m<sup>3</sup>) at **standard** temperature and pressure (25-C and 760 mm Hg), Section 17.1.3.

17.3 Sample Concentration Conversion From **ng/m<sup>3</sup>** to ppbv

17.3.1 The concentrations calculated in Section 17.2 can be converted to ppbv for general reference.

17.3.2 The analyte concentration can **be** converted to ppbv using the following equation:

$$C(A)(\text{ppbv}) = C(A) (\text{ng/m}^3) * \frac{24.4}{\text{MW}(A)}$$

where:

C(A) = concentration of analyte, **ng/m<sup>3</sup>**, calculated according to Sections 17.2.1 through 17.2.3.

MW(A) = molecular weight of analyte, g/g-mole

24.4 = molar volume occupied by **ideal** gas at standard temperature and pressure (25-C and 760 mm Hg), l/mole.

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TABLE 1. **FORMULAE AND PHYSICAL PROPERTIES OF SELECTIVE PAHs**

	FORMULA	MOLECULAR WEIGHT	MELTING POINT C	BOILING POINT C	CASE #
Acenaphthene	<b>C12H10</b>	154.21	96.2-	279	83-32-9
Acenaphthylene	<b>C12H8</b>	152.20	92-93	<b>265-275</b>	<b>208-96-8</b>
Anthracene	<b>C14H10</b>	178.22	<b>218-</b>	342	120-12-7
Benzo (a) anthracene	<b>C18H12</b>	228.29	<b>158-159</b>	-	<b>56-55-3</b>

Benzo (a) pyrene	C20H12	252.32	177-	310-312	50-32-E
Benzo (b) fluoranthene	C20H12	252.32	168	-	205-99-2
Benzo (e) pyrene	C20H12	252.32	178-179	-	192-92-2
Benzo (g, h, i) perylene	C22H12	276.34	273	-	191-24-2
Benzo (k) fluoranthene	C20H12	252.32	217	480	207-08-g
Chrysene	C18H12	228.29	255-256		218-01-g
Dibenzo (a, h) anthracene	C22H14	278.35	262		53-70-3
Fluoranthene	C16H10	202.26	110		206-44-o
Fluorene	C13H10	166.22	116-117	293-295	86-73-7
Indeno (1,2,3-cd) pyrene	C22H12	276.34	161.5-163		193-39-S
Naphthalene	C10H8	128.16	80.2	217.9	91-20-3
Phenanthrene	C14H10	178.22	100-	340	85-01-8
Pyrene	C16H10	202.26	156	399	129-00-0

\* Many of these compounds sublime.

TABLE 2. RETENTION TIMES FOR SELECTIVE PAHs FOR PACKED AND CAPILLARY COLUMNS

Compound	Packed(1)	Capillary(2)
Acenaphthene	10.8	16.8
Acenaphthylene	10.4	15.9
Anthracene	15.9	20.7
Benzo (a) anthracene	20.6	29.1
Benzo (a) pyrene	29.4	36.2
Benzo (b) fluoranthene	28.0	34.2
Benzo (ghi) perylene	38.6	48.4
Benzo (k) fluoranthene	28.0	34.4
Chrysene	24.7	29.3
Dibenzo (a, h) anthracene	36.2	46.1
Fluoranthene	19.8	24.3
Fluorene	12.6	18.1
Indeno (1,2,3-cd) pyrene	36.2	45.6
Naphthalene	4.5	11.0
Phenanthrene	15.9	20.6
Pyrene	20.6	25.0

- (1) GC conditions: Chromosorb W-AW-DMCS (100/120 mesh) coated with 3% OV-17, packed in a 1.8-m long x 2 mm ID glass column, with nitrogen carrier gas at a flow rate of 40 mL/min. Column temperature was held at 100-C for 4 min. then programmed at 8 degrees/minute to a final hold at 280-C.
- (2) Capillary GC conditions: 30 meter fused silica SPB-5 capillary column; flame ionization detector, splitless injection; oven temperature held at 80 degrees C for 2 minutes, increased at 8 degrees/min. to 280 degrees C.

TABLE 3. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

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

TABLE 4. GC AND MS OPERATING CONDITIONS

Chromatography

Column	Hewlett-Packard Ultra #2 crosslinked 5% phenyl methyl silicone (50 m x 0.25 mm, 0.25 $\mu$ m film thickness) or equivalent.
Carrier Gas	Helium velocity 20 cm <sup>3</sup> /sec at 250-C
Injection Volume	Constant (1-3 $\mu$ L)
Injection Mode	Splitless

Temperature Program

Initial Column Temperature	45-c
Initial Hold Time	1 min
Program	45-C to 100-C in 5 min, then 100-C to 320-C at 8-C/min
Final Hold Time	15 min

Mass Spectrometer

Detection Mode	Multiple ion detection, SIM mode
----------------	----------------------------------

TABLE 5. CHARACTERISTIC IONS FROM GC/MS DETECTION FOR DEUTERATED INTERNAL STANDARDS AND SELECTED PAHs

Compound	M/Z
----------	-----

Dg-naphthalene	136
D10-phenanthrene	188
phenanthrene	178
anthracene	178
Fluoranthene	202
D10-pyrene	212
Pyrene	202
Cyclopenta [c, d] pyrene	226
Benz[a]anthracene	228
D12-chrysene	240
Benzo[e]pyrene	252
D12-benzo[a]pyrene	264
Benzo[a]pyrene	252

-----

TABLE 6. CHARACTERISTIC IONS FROM GC/MS DETECTION FOR SELECTED PAHs

Compound	Primary		Secondary
Acenaphthene	154	<b>153</b>	152
Acenaphthylene	<b>152</b>	151	153
Anthracene	178	179	176
Benzo (a) anthracene	228	229	226
Benzo (a) pyrene	<b>252</b>	253	125
Benzo (b) fluoranthene	<b>252</b>	253	125
Benzo (ghi) perylene	276	138	277
Benzo (k) fluoranthene	<b>252</b>	253	125
Cibenzo (a, h) anthracene	228 270	226 139	229 279
luoranthene	202	101	203
Fluorene	166	165	167
Indeno (1, 2, 3-cd) pyrene	276	138	227
Naphthalene	128	129	127
Phenanthrene	178	179	176
Pyrene	202	200	203

-----

TABLE 7. COMMERCIAL AVAILABLE COLUMNS FOR PAH ANALYSIS USING HPLC

company	Column Identification	Column Name
The Separation Group P.O. Box 867 Hesperia, California 92345	<b>201-TP</b>	<b>VYDAC</b>
Rainin Instrument Company Mack Road Wasurn, MA 01801-4626	Ultrasphere - ODS	ALEX
Supelco, Inc. Supelco Park	<b>LC-PAH</b>	Supelcosil

Bellefonte, PA 16823-0048

DuPont Company  
Technology Systems  
Larley Mill Plaza, P24  
Wilmington, DE 19898

ODS

Zorbax

Perkin-Elmer Corp.  
Corporate Office  
Main Avenue Norwalk, CT 06856

HC-ODS

Sil-X

Waters Associates  
34-T Maple St.  
Milford, MA 01757

u-Bondapak

NH3 u-Bondapak

TABLE 8. TYPICAL RETENTION TIME FOR SELECTIVE PAHs BY HPLC SEPARATION AND DETECTION

Compound	Retention Times (minutes)			
	HPLC Conditions			
	Condition A		Condition B	
	Fluorescence	W	Fluorescence	W
Acenaphthene		20.5		18.0
Acenaphthylene		18.5		15.0
Anthracene	23.4		21.0	21.0
Benzo(a)anthracene	28.5		26.3	26.3
Benzo(a)pyrene	33.9		31.1	31.1
Benzo(b)fluoranthene	31.6		29.3	29.3
Benzo(e)pyrene			31.1	
Benzo(ghi)perylene	36.3		33.9	33.9
Benzo(k)fluoranthene	32.9		30.2	30.2
Chrysene	29.3		26.7	
Dibenzo(a,h)anthracene	35.7		32.7	32.7
Fluoranthene	24.5		22.5	22.5
Fluorene		21.2	18.5	18.5
Indeno(1,2,3-cd)pyrene	37.4		34.6	34.6
Naphthalene		16.6		14.0
Phenanthrene	22.1		19.9	19.9
Pyrene	25.4		23.4	23.4

Condition A

HPLC parameters: Reverse phase HC-ODS Sil-X, 5 micron particle size, in a 250-mm x 2.6-m I.D. stainless steel column. Isocratic elution for 5 min using acetonitrile/water (4:6)(v/v), then linear gradient elution to 100% acetonitrile over 25 min at 0.5 mL/min flow rate. If columns having other internal diameters are used, the flow rate should be adjusted to maintain a linear velocity of 2 mm/sec.

Condition B

HPLC parameters: Reverse phase VYDAC 201 TP 5415, 5 micron particle size,

in a .46 x 25 cm stainless steel column. Isocratic elution for 10 min using acetonitrile/water (4:6) (v/v), then linear gradient elution to 100% acetonitrile for 10 minutes then linear gradient to 40/60 acetonitrile for 15 minutes at 15 mL/min.

TABLE 9. RETENTION TIMES (RT) AND **MINIMUM** DETECTION LIMITS (MDLs) FOR SELECTED **PAHs** USING ULTRAVIOLET AND FLORESCENCE DETECTION

PAH	Ultraviolet Detector		Florescence Detector	
	RT	MDL	RT	MDL
Naphthalene	14.0	250pg/uL		
Acenaphthylene	15.85	250pg/uL		
Acenaphthene	18.0	250pg/uL		
Fluorene	18.5	50pg/uL	18.5	5pg/uL
Phenanthrene	19.9	mpg / -	19.9	10pg/uL
Anthracene	21.0	50pg/uL	21.0	50pg/uL
Fluoranthene	22.5	50pg/uL	22.5	10pg/uL
Pyrene	23.4	50pg/uL	23.4	5pg/uL
Benzo (a) anthracene	26.3	50pg/uL	26.3	5pg/uL
Chrysene	26.7	50pg/uL	26.7	5pg/uL
Benzo (b) fluoranthene	29.3	50pg/uL	29.3	10pg/uL
Benzo (k) fluoranthene	30.2	50pg/uL	30.2	5pg/uL
Benzo (a) pyrene	31.1	50pg/uL	31.1	5pg/uL
Dibenzo (a, h) anthracene	32.7	50pg/uL	32.7	5pg/uL
Benzo (ghi) perylene	33.9	50pg/uL	33.9	5pg/uL
Indeno (1, 2, 3 -cd) pyrene	34.6	50pg/uL	34.6	50pg/uL

RT = Retention time in minutes

MDL = Minimum detection limit



Final Rpt, Kuwait Oil Fire. HRA No. 39-26-L192-91, 5 May - 3 Dec 91

ANNEX E-5

E-5-1

**SOP NUMBER 147.1**  
**OCTOBER 1993**

**STANDING OPERATING PROCEDURE**  
**ORGANIC ENVIRONMENTAL CHEMISTRY DIVISION**

**DETERMINATION OF HEXAVALENT CHROMIUM**  
**IN SOIL**

DEPARTMENT OF THE ARMY  
 U.S. ARMY ENVIRONMENTAL HYGIENE AGENCY  
 ORGANIC ENVIRONMENTAL CHEMISTRY DIVISION  
 ABERDEEN PROVING GROUND, MARYLAND 21010-5423

HSHB-ML-O

OCTOBER 1993

STANDING OPERATING PROCEDURE NUMBER 147.1

**DETERMINATION OF HEXAVALENT CHROMIUM IN SOIL,**

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PRECISION AND ACCURACY .....	4	2
<b>SENSITIVITY AND LINEARITY</b> .....	5	2
<b>EQUIPMENT</b> .....	6	2
REAGENTS .....	7	2
PROCEDURES .....	8	2
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<b>REFERENCES</b> .....	10	5

1. **INTRODUCTION.** This Standing **Operating** Procedure (SOP) describes a procedure for the detection and **quantitation** of low levels of dissolved hexavalent chromium in soil using a HACH field screening kit Cat. #24618-00.

2. **PRINCIPLE.** Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as iron, vanadium, mercury and molybdenum, may be determined calorimetrically by reaction with diphenylcarbazide in acid solution. A redviolet color of unknown composition is **produced**. The intensity of this color **is** measured at 540 nm. This HACH kit only responds to soluble hexavalent chromium salts that are **solubilized** in the **alkaline** extraction process and by no means be **misconstrued** as providing total hexavalent chromium results.

3. **INTERFERENCES.** The chromium **reaction** with **diphenylcarbazide** is **specific** for the hexavalent species. **Molybdenum** and mercury salts also **react** to form color with the reagents, **however** the color intensities produced are reported to **be** much lower than those for chromium at the **specific pH**. Vanadium interferes strongly, but **concentrations** up to 10X that of chromium will not cause trouble. Iron in concentrations greater than 1 mg/L may produce a yellow color and is not absorbed at the appropriate wavelength.

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4. **PRECISION AND ACCURACY.** The accuracy and the precision of the procedure **has** not been completely determined. Recovery obtained from spiked sandy soils ranged from **80-100%** with a mean value of 94%. from a concentration range from 0.4 to 1.6 ppm. Recoveries **from** 80% to 100% were obtained in a concentration **range** from 0.1 to 1.2 ppm **with a mean of 91%**.

5. **SENSITIVITY AND LINEARITY.** An estimated detection limit of 0.1 ppm was achieved with several spikes. Calibration **curves** were **linear** over the investigated range from 0.1 to 1.5 ppm.

6. **EQUIPMENT.**

a. Volumetric flasks and **pipets** for preparing standards; sizes will vary according to the **range** to be **measured**.

b. A variable **μL pipet** for sample spiking and **standard preparations**.

c. A **spectrophotometer** capable of measuring **at 540 nm** equipped with a 1 cm cell path length.

d. 1 cm **cuvettes**.

e. HACH field test kit Cat. **#24618-00**.

7. **REAGENTS AND CHEMICALS.**

a. All chemicals required for this test are provided **as part** of the **HACH** field test kit.

b. High purity water, **ASTM type II** water (ASTM 01193).

8. **PROCEDURES.**

a. **Safety.** Hexavalent chromium is toxic by **inhalation** as well **as** by ingestion; work with the neat **chemical** should be conducted within a **fume** hood while wearing appropriate personal protective equipment.

b. **Sample Preparation** be submitted in glass jars with teflon-lined caps. Analysis of the **samples** is conducted within 24 hours following. It is recommended that the analysis be conducted in the field **as** samples are received.

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c. standards.

(1) A **stock** standard is provided in the kit that contains 50 **mg/L** hexavalent chromium. This stock standard is used to prepare working standards and calibration **curves** as well as for standard additions.

(2) Serial dilutions may be made from the stock standard to prepare solutions in the range of interest. At **least** three standards should be run to verify **linearity** of response. A typical set of standards might contain 125, 250, 500, 1000 and 1250 **ng/g** chromium **in** soil. A detection level standard should also be prepared for each set of samples to be analyzed. Working standards should be prepared fresh daily.

d. Instrument Setup.

(1) The **spectrophotometer** is set to read absorbance at a wave length of 540 **nm**. The instrument is zeroed and calibrated according to and following the manufactures procedures as provided in the **operations** manual.

(2) The HACH kit is also used in accordance with the procedures provided with the kit.

e. Quality Control.

(1) A series of standards (three or more concentration levels) are analyzed before running any samples. The resultant standard curve should give a **linearity** of 0.995 or better; if linearity is not achieved, new standards should be prepared and **analyzed**.

(2) The analytical technique of standard additions is used to demonstrate the matrix affects of each sample analyzed,

f. Analysis.

(1) The instrument is setup and the standards prepared.

(2) There are several problem **areas associated** with the analysis of hexavalent chromium **in** soil:

(a) An **alkaline extraction** is used to remove the water soluble hexavalent chromium salts from the soil which is accomplished at an approximate **pH** 10. Extraction reagent packets are provided in the **HACH** kit.

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(b) The color complex formed with the **diphenylcarbazide** occurs only at a **pH** of 1-2 and this **pH** must be checked to insure complete color development.

(c) Following extraction the sample requires **filtration** for the removal of suspended particles.

(d) A sample blank which does not contain the color reagent is required to be analyzed with each sample in order to subtract out the blanks absorbance.

(e) Three standard additions at the sample concentration is made to each sample and the results recorded. If the sample is **blank**, then three concentrations equal to the concentration of the lowest standard used in the calibration **curve** is added to the sample and the matrix **affects** determined.

(3) 20 grams of the sample is weighed into the provided whirl-pak bags.

(4) 40 **mL** of **ASTM Type II** deionized water containing one dissolved **extraction reagent pillow is** added to the sample and sample the bag **sealed**.

(5) Shake the extraction solution for 15 seconds **at 2 minute intervals** for a period of 15 **minutes**.

(6) Set up a filtering funnel with the fluted **filter paper** provided in the kit and filter the 40 **mL** of sample into a 50 **mL graduated** cylinder.

(7) Remove two 10 **mL aliquots** of the sample filtrate and bring each to a 25 **mL final** volume with **ASTM Type II** deionized water in two separate 25 **mL graduated** cylinders. One sample serves as a blank.

(8) Add the contents of the **chromium** reagent powder pillow to one of the 25 **mL graduated** cylinders containing the filtered sample. The contents of the other cylinder as stated above **serves as** a blank. Allow a **10-minute reaction** period for color development.

(9) Pour the prepared sample that had the color reagent pillow added to the top mark of one of the plastic viewing tubes provided in the kit and pour the blank sample to the top mark of the other viewing tube to **serve as** the blank.

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(10) Make certain that the color viewer is set up with the long path viewing adapter and the color disk installed in the viewing **box**.

(11) Place the blank **tube** into the blank position of the comparator. Place the viewing tube with the prepared sample into the sample position. orient the **comparator** with the tube tops pointing toward a light **source**. **Turn** the color wheel until the color on the wheel matches the color of the prepared sample tube.

(12) Read the **mg/L** on the color disk scale and convert to actual **mg/L** using the conversion chart provided in the instruction manual found **in each** kit.

9. CALCULATIONS. The amount of hexavalent chromium found in each sample extract may **be read** directly as **mg/L** hexavalent chromium from the conversion chart provided in each kit or from the absorbance **obtained** from a calibration **curve**. Calculations necessary to obtain ppm concentrations **in** soil are obtained using the following formulae:

$$\text{Cr6+ ppm} = \frac{\text{Disk Reading (mg/L)} \times 1000}{\text{Aliquot Volume (mL)} \times \text{Sample Size (grams)}}$$

#### 10. REFERENCES.

a. SW - 846 Third Edition, September 1986 Method **#7196, Colorimetric** Procedure for the Determination of Hexavalent Chromium **& Method #3060, Alkaline** Digestion of Solid Waste Samples for Hexavalent Chromium.

b. **DeYong, Gregory D.**, et. al., Determination of **Hexavalent** Chromium in Soil Samples, **Superfund** 1990, **Proceedings** of the 11th National Conference.

c. Deyong, Gregory D., et. al., Field Analysis For Hexavalent Chrome In Soil, HACH Corporation, Ames, Iowa.



Final Rpt, Kuwait Oil Fii HRA No. 39-26-L192-91, 5 May - 3 Dec 91

ANNEX E-6

E-6-1

**HSHB-ML-RM**

Radiological and Inorganic Chemistry Division  
Metals Analysis **Branch**

STANDARD OPERATING PROCEDURE  
for  
ACID DIGESTION OF SEDIMENT, SLUDGES, AND **SOILS**

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

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

II. PURPOSE, This procedure is used to digest sediments, sludges, and soils and produce a liquid that will be **acceptable** for the instrument of choice.

III. PRINCIPLES. A representative 1 to 2 **g** (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then **refluxed** with either **nitric** or hydrochloric acid. Hydrochloric acid is used for Flame **AA** and nitric acid is used for Furnace **AA** work. A separate sample shall be dried for a total **% solids** determination.

IV. LOCATION. This SOP will be used in the Metals Analysis Branch's preparation laboratory. The SOP will be distributed to all **MAB** personnel who perform sample prep techniques.

V. **INTERFERENCES**. Sludge samples **can** contain diverse matrix types, each of which may present its own analytical challenge.

VI. **QUALITY CONTROL**. For each batch of samples processed, a reagent blank should **be** carried throughout the entire **sample-preparation** and analytical process. These blanks are useful **in determining** if samples are being contaminated.

Replicate samples should be processed on a routine basis (about 10 %). This sample **is** to be carried throughout the entire sample-preparation and analytical process.

Spiked samples or standard reference materials should be employed to determine accuracy. This should **be** about 3% of the total number of samples.

#### VII. EQUIPMENT.

- A. Griffin **beaker** - 150 - 200 **mL** or equivalent.
- B. Watch glass - Ribbed.
- C. Graduated cylinder or equivalent - 100 **mL**.
- D. Filtering Apparatus - **Millipore** or equivalent.
- E. Qualitative **filter** paper to place in filtering apparatus.
- F. Drying oven - That can be maintained at 30 °C.
- G. Analytical Balance - Accurate to **0.01 g**.

#### VIII. REAGENTS and CHEMICALS.

- A. Deionized Water (**DI**) - ASTM Type I quality or better.
- B. Nitric acid **HNO<sub>3</sub>** (concentrated) - ACS reagent **grade** or better.
- C. Hydrochloric acid **HCl (concentrated)** - ACS reagent grade or better.
- D. Hydrogen Peroxide **H<sub>2</sub>O<sub>2</sub>** (30%) - **Analytical** grade.
- E. Potassium Iodide (**KI**) - ACS reagent grade or better.
- F. Iodine (**I<sub>2</sub>**) - ACS reagent grade, or better.
- G. Ammonium hydroxide **NH<sub>4</sub>OH** - concentrated ACS grade or better.

## IX. PROCEDURE.

A. Safety. When preparing the acid standard, always add acid to water. While working with **any** acids, wear protective equipment (safety glasses, lab coat, and gloves).

### B. Preparation of Reagents.

1. **1:1 HNO<sub>3</sub>** reagent is prepared by putting about 350 **mLs** of deionized water into a 1 L volumetric. Slowly add 500 **mL** of concentrated nitric acid. Bring up to volume with DI water.
2. Iodine solution (IN). Dissolve 20.9 **KI** in 50 **mL** water in the 100 **mL** flask. Add 12.7 g iodine and bring up to volume with DI water. Store solution in a brown bottle.
3. Cyanogen Iodide solution is prepared by mixing 50 **mL** DI water, 4.3 **mL conc. NH<sub>4</sub>OH**, 6.5 **g KCN**, and 5.0 **mL** iodine solution into a 100 **mL** volumetric flask. Bring up to volume with DI water and stored in a brown bottle.

C. Standards. See **the instrument** SOP for the **preparation** of the standards.

### D. Analysis.

1. Mix the sample 'thoroughly to **achieve** homogeneity. For each digestion procedure, weigh to the nearest 0.01 **g** and transfer to a **griffin** beaker 1.00-2.00 **g** of sample. For samples with low percent solids a larger- sample site may be used as long as digestion is complete.
2. Add 10 **mL** of **1:1 HNO<sub>3</sub>**, mix the slurry, and cover with a watch glass. Heat sample to 95 °C and reflux for 10 to 15 minutes without boiling.
3. Allow sample to cool, add 5 **mL** of concentrated **HNO<sub>3</sub>**, replace the watchglass, and reflux for 30 minutes. **Repeat** this last step to ensure complete oxidation. a ribbed watchglass, allow the solution to evaporate to 5-10 **mLs** (maintain enough solution to cover the bottom of the beaker) without boiling.
4. Cool the sample and add 2 **mL** of DI water and 3 **mL** of **30X H<sub>2</sub>O<sub>2</sub>**. Cover the beaker with a watchglass and **return** to the hot plate for warming and start the **peroxide** reaction. Note: Care must **be** taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until **effervescence** subsides and **cool** beaker.
5. Continue adding 30 % **H<sub>2</sub>O<sub>2</sub>** in 1 **mL aliquots** with **warming** until the **effervescence** is minimal or until the sample appearance is unchanged. Note: Do not add more than 10 **mL** of 30% **H<sub>2</sub>O<sub>2</sub>**.
6. For ICP analysis: Add 5 **mL** of concentrated **HCl** and 10 **mL** of water, **return** to the hotplate, and reflux for an additional 15 minutes.
7. Filter or centrifuge the digestate. Bring up to volume (100 **mLs**) with DI water. Pour into plastic sample bottles and label sample with AQAD number and "A."

8. For Furnace analysis: Continue heating the **sample** with a ribbed watchglass until the volume is 5-10 **mL** without boiling. Cool sample and follow step #7 except label bottles with a "B."

9. If plating out of **AgCl** is suspected, another aliquot must be prepped. Redo steps 1 through 7 and then the precipitant can be redissolved by neutralizing the sample, adding 1 **mL cyanogen** iodide to the sample and bringing up to volume with DI water. This can be done **only** after neutralization of the sample to a **pH > 7** to prevent formation of toxic cyanide under acid conditions.

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

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

#### XI. REFERENCES.

A. Test Methods for **Evaluating** Solid Waste, SW-846, Jan 1990, **Method 3050A** (Acid Digestion of Sediments, Sludges, and Soils).

2. Test Methods for **Evaluating** Solid Waste, SW-846, Jan 1990, **Method 7761 (Silver-GFAA)**.



Final Rpt, Kuwait Oil Fire HRA No. 39-26-L192-91, 5 May - 3 Dec 91

ANNEX E-7

E-7-1

## METHOD 6010A

### INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY

#### 1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-atomic emission **spectroscopy (ICP)** determines trace elements, including **metals**, in solution. The method is **applicable** to all of the elements listed in Table 1. All matrices, including ground water, aqueous samples, TCLP and **EP** extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.

1.2 Elements for which Method **6010A** is **applicable** are listed in Table 1. **Detection** limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of spectrometer. The data shown in Table 1 provide concentration ranges for clean aqueous samples. Use of this method is restricted to spectroscopists who are **knowledgeable** in the co&on of spectral, chemical, and physical interferences.

#### 2.0 SUMMARY OF **METHOD**

2.1 Prior to analysis, samples must be **solubilized** or digested using appropriate Sample Preparation Methods (e.g., Methods **3005A-3050A**). When analyzing for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 Method **6010A** describes the simultaneous, or sequential, multielemental determination of elements by ICP. The method measures elementemitted light by optical **spectrometry**. Samples **are nebulized** and the resulting aerosol is transported to the plasma torch. **Element-specific** atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The **spectra** are dispersed by a grating spectrometer, and the intensities of the lines **are** monitored by photomultiplier tubes. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the **analytical** line, will be determined by the complexity of the **spectrum** adjacent to the analyte line. The position used must be free of **spectral interference** and reflect the **same** change in background intensity as occurs at the analyte wavelength measured. Background **correction** is not required in cases of line broadening **where** a background correction measurement would actually degrade the

analytical result, The possibility of additional interferences named in Section 3.0 should also be **recognized** and appropriate corrections made; tests for their presence are described in Step 8.5.

### 3.0 INTERFERENCES

3.1 **Spectral** interferences **are** caused by: (1) overlap of a **spectral** line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap **can** be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the **analyte**

Users of simultaneous multielement instruments must verify the absence of **spectral** interference from an element in a sample for which there is no instrument detection channel. Potential **spectral** interferences for the recommended wavelengths **are** given **in** Table 2. The data in Table 2 are intended as rudimentary guides for **indicating** potential interferences; for this purpose, **linear** relations between concentration and intensity for the **analytes** and the **interferents can** be assumed.

3.1.1 The interference is expressed as analyte concentration equivalents (i.e., false **analyte** concentrations) arising from 100 **mg/L** of the **interference** element. For example, assume that As is to be determined (at 193.696 **nm**) in a sample **containing** approximately 10 **mg/L** of Al. According to Table 2, 100 **mg/L** of Al would yield a false signal for As equivalent to approximately 1.3 **mg/L**. **Therefore**, the presence of 10 **mg/L** of Al would result **in** a false signal for As equivalent to approximately 0.13 **mg/L**. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be **evaluated** for each individual instrument since the intensities will vary with operating conditions, power, viewing height, argon flow rate, etc.

3.1.2 The dashes **in** Table 2 indicate that no measurable interferences were **observed** even at higher **interferent** concentrations. Generally, interferences were **discernible** if they produced **peaks**, or background shifts, **corresponding** to 2 to 5 % of the p&s generated by the analyte **concentrations**.

3.1.3 At present, information on the listed silver and potassium wavelengths is not available, but it has been reported that second-order energy from the magnesium 383.23 **1-nm** wavelength interferes with the listed potassium **line** at 766.491 **nm**.

TABLE 1.  
RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Detection Element	Wavelength <sup>a</sup> (nm)	Estimated Limit <sup>b</sup> (ug/L)
Aluminum	308.215	45
Antimony	206.833	32
Arsenic	193.696	53
Barium	455.402	2
Bismuth	455.402	0.3
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716 228.616	7
Cobalt		7
Copper	324.754 259.940	67
Iron	220.353	42
Lithium	670.784	5
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	a
Nickel	213.608	15
Phosphorus	213.608	51
Potassium	766.491	See note c
Selenium	196.026	75
Silver	328.068	7
Sodium	588.995	29
Strontium	407.771	0.3
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

<sup>a</sup>The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Step 3.1). In time, other elements may be added as more information becomes available and as required.

<sup>b</sup>The estimated instrumental detection limits shown are taken from Reference 1 in Section 10.0 below. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

<sup>c</sup>Highly dependent on operating conditions and plasma position.

TABLE 2.

## ANALYTE CONCENTRATION EQUIVALENTS ARISING FROM INTERFERENCE AT THE 100-mg/L LEVEL

Analyte	Wavelength (nm)	Interferent <sup>a,b</sup>									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Tl	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

<sup>a</sup>Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

Al - 1000 mg/L	Mg - 1000 mg/L
Ca - 1000 mg/L	Mn - 200 mg/L
Cr - 200 mg/L	Tl - 200 mg/L
cu - 200 mg/L	v - 200 mg/L
Fe - 1000 mg/L	

<sup>b</sup>The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferent figure.

3.2 Physical interferences **are** effects associated with the sample **nebulization** and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample or by using a peristaltic pump. Another problem that can occur with high dissolved solids is salt buildup **at** the tip of the nebulizer, which affects aerosol flow rate and causes **instrumental** drift. The problem can **be** controlled by wetting the argon prior to **nebulization**, using a tip washer, or diluting the sample. **Also**, it has been **reported** that better control of the argon flow rate improves instrument performance; this is accomplished with the use of mass flow controllers.

3.3 Chemical interferences include molecular compound formation, ionization effects, and solute **vaporization** effects. **Normally**, these effects are not **significant** with the ICP **technique**. If **observed**, they **can** be minimized by careful selection of operating conditions (incident power, **observation** position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. **Chemical** interferences are highly dependent on matrix **type** and the **specific analyte** element.

#### 4.0 APPARATUS AND **MATERIALS**

##### 4.1 Inductively coupled argon plasma **emission spectrometer**:

- 4.1.1 **Computer-controlled** emission spectrometer with background correction.
- 4.1.2 Radio frequency generator compliant with FCC regulations.
- 4.1.3 **Argon gas** supply - Welding **grade** or better.

4.2 Operating conditions - The analyst should follow the instructions provided by the instrument manufacturer. For operation with organic solvents, use of the auxiliary argon **inlet is** recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual **analyte** line on that particular instrument. All **measurements** must be within the instrument **linear range** where coordination factors are valid. The analyst must (1) verify that the **instrument configuration** and **operating** conditions satisfy the **analytical** requirements and (2) maintain quality control data **confirming** instrument performance and **analytical** results.

##### 4.3 Class A volumetric flasks

#### 4.4 Class A volumetric pipets

### 5.0 REAGENTS

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

#### 5.1.1 Hydrochloric acid (**conc**), **HCl**.

5.1.2 Hydrochloric acid (1: 1), **HCl**. Add 500 **mL** concentrated **HCl** to 400 **mL** water and dilute to 1 liter in an appropriate beaker.

#### 5.1.3 Nitric acid (**conc**), **HNO<sub>3</sub>**.

5.1.4 Nitric acid (1:1), **HNO<sub>3</sub>**. Add 500 **mL** concentrated **HNO<sub>3</sub>** to 400 **mL** water and dilute to 1 liter in an **appropriate** beaker.

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

5.3 Standard stock solutions may be purchased or **prepared** from ultrahigh purity grade chemicals or metals (99.99 to 99.999 % pure). All salts must be dried for 1 hour at 105 ° C, unless otherwise specified.

**CAUTION:** Many metal salts **are** extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure metal added, or with the use of the mole fraction and the weight of the metal salt added.

Metal

$$\text{Concentration (ppm)} = \frac{\text{Weight (mg)}}{\text{volume (L)}}$$

## Metal salts

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)} \times \text{mole fraction}}{\text{volume (L)}}$$

5.3.1 **Aluminum** solution; stock, 1 mL = 1000 ug Al: Dissolve 1.0 g of **aluminum** metal, weighed **accurately** to at **least** four significant figures, in an acid mixture of 4 mL of (1:1) **HCl** and 1 mL of concentrated **HN03** in a **beaker**. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of (1:1) **HCl** and dilute to volume in a 1,000 mL volumetric **flask** with **water**.

5.3.2 Antimony solution, stock, 1 mL = 1000 ug Sb: Dissolve 2.70 g **K(SbO)C4H4O6** (mole fraction Sb = **0.3749**), weighed accurately to at least four significant figures, in water, add 10 mL (1: 1) **HCl**, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.3 Arsenic solution, stock, 1 mL = 1000 ug **As**: Dissolve 1.30 g of **As2O3** (mole fraction **As** = **0.7574**), weighed accurately to at least four **significant** figures, in 100 mL of water containing 0.4 g **NaOH**. Acidify the solution with 2 mL concentrated **HN03** and dilute to volume in a 1,000 mL volumetric **flask** with water

5.3.4 Barium solution, stock, 1 mL = 1000 ug **Ba**: Dissolve 1.50 g **BaCl2** (mole fraction **Ba** = **0.6595**), dried at 250°C for 2 hours, weighed accurately to at least four **significant** figures, in 10 mL water with 1 mL (1:1) **HCl**. Add 10.0 mL (1:1) **HCl** and dilute to volume in a 1,000 mL volumetric **flask** with water.

5.3.5 Beryllium solution, stock, 1 mL = 1000 ug Be: Do not dry. Dissolve 19.7 g **BeSO4 4H2O** (mole fraction Be = **0.0509**), weighed accurately to at least four significant figures, in water, add 10.0 mL concentrated **HN03**, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.6 Cadmium solution, stock, 1 mL = 1000 ug Cd: Dissolve 1.10 g **CdO** (mole fraction Cd = **0.8754**), weighed accurately to at least four **significant** figures, in a minimum amount of (1: 1) **HNO3**. Heat to **increase** rate of dissolution. Add 10.0 mL concentrated **HN03** and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.7 Calcium solution, stock, 1 mL = 1000 ug **Ca**: Suspend 2.50 g **CaCO3** (mole **Ca fraction** = **0.4005**), dried at 180°C for 1 hour before weighing, weighed accurately to at least four **significant** figures, in water and dissolve cautiously with a minimum amount of (1: 1) **HNO3**. Add 10.0 mL concentrated **HN03** and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.8 Chromium solution, stock, 1 mL = 1000 ug Cr: Dissolve 1.909 CrO<sub>3</sub> (mole fraction Cr = 0.5200), weighed accurately to at least four significant figures, in water. When solution is complete, acidify with 10 mL concentrated HNO<sub>3</sub> and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.9 Cobalt solution, stock, 1 mL = 1000 ug Co: Dissolve 1.009 of cobalt metal, weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO<sub>3</sub>. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.10 Copper solution, stock, 1 mL = 1000 ug Cu: Dissolve 1.309 CuO (mole fraction Cu = 0.7989), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO<sub>3</sub>. Add 10.0 mL concentrated HNO<sub>3</sub> and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.11 Iron solution, stock, 1 mL = 1000 ug Fe: Dissolve 1.409 Fe<sub>2</sub>O<sub>3</sub> (mole fraction Fe = 0.6994), weighed accurately to at least four significant figures, in a warm mixture of 20 mL (1:1) HCl and 2 mL of concentrated HNO<sub>3</sub>. Cool, add an additional 5.0 mL of concentrated HNO<sub>3</sub>, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.12 Lead solution, stock, 1 mL = 1000 ug Pb: Dissolve 1.609 Pb(NO<sub>3</sub>)<sub>2</sub> (mole fraction Pb = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO<sub>3</sub>. Add 10 mL (1:1) HNO<sub>3</sub> and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.13 Lithium solution, stock, 1 mL = 1000 ug Li: Dissolve 5.3249 lithium carbonate (mole fraction Li = 0.1878), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.14 Magnesium solution, stock, 1 mL = 1000 ug Mg: Dissolve 1.709 MgO (mole fraction Mg = 0.6030), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO<sub>3</sub>. Add 10.0 mL (1:1) concentrated HNO<sub>3</sub> and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.15 Manganese solution, stock, 1 mL = 1000 ug Mn: Dissolve 1.009 of manganese metal, weighed accurately to at least four significant figures, in acid mixture (10 mL concentrated HCl and 1 mL concentrated HNO<sub>3</sub>) and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.16 Molybdenum solution, stock, 1 mL = 1000 ug Mo: Dissolve 2.00 g  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  (mole fraction Mo = 0.5772), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.17 Nickel solution, stock, 1 mL = 1000 ug Ni: Dissolve 1.00 g of nickel metal, weighed accurately to at least four significant figures, in 10.0 mL hot concentrated  $\text{HNO}_3$ , cool, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.18 Phosphate solution, stock, 1 mL = 1000 ug P: Dissolve 4.393 g anhydrous  $\text{KH}_2\text{PO}_4$  (mole fraction P = 0.2276), weighed accurately to at least four significant figures, in water. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.19 Potassium solution, stock, 1 mL = 1000 ug K: Dissolve 1.90 g  $\text{KCl}$  (mole fraction K = 0.5244) dried at  $110^\circ\text{C}$ , weighed accurately to at least four significant figures, in water, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.20 Selenium solution, stock, 1 mL = 1000 ug Se: Do not dry. Dissolve 1.70 g  $\text{H}_2\text{SeO}_3$  (mole fraction Se = 0.6123), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.21 Silver solution, stock, 1 mL = 1000 ug Ag: Dissolve 1.60 g  $\text{AgNO}_3$  (mole fraction Ag = 0.6350), weighed accurately to at least four significant figures, in water and 10 mL concentrated  $\text{HNO}_3$ . Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.22 Sodium solution, stock, 1 mL = 1000 ug Na: Dissolve 2.50 g  $\text{NaCl}$  (mole fraction Na = 0.3934), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated  $\text{HNO}_3$  and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.23 Strontium solution, stock, 1 mL = 1000 ug Sr: Dissolve 2.415 g of strontium nitrate ( $\text{Sr}(\text{NO}_3)_2$ ) (mole fraction 0.4140), weighed accurately to at least four significant figures, in a 1-liter flask containing 10 mL of concentrated  $\text{HCl}$  and 700 mL of water. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.24 Thallium solution, stock, 1 mL = 1000 ug Tl: Dissolve 1.30 g  $\text{TlNO}_3$  (mole fraction Tl = 0.7672), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated  $\text{HNO}_3$  and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.25 Vanadium solution, stock, 1 mL = 1000 ug V: Dissolve 2.309 NH<sub>4</sub>VO<sub>3</sub> (mole fraction V = 0.4356), weighed accurately to at least four significant figures, in a minimum amount of concentrated HNO<sub>3</sub>. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO<sub>3</sub> and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.26 Zinc solution, stock, 1 mL = 1000 ug Zn: Dissolve 1.209 ZnO (mole fraction Zn = 0.8034), weighed accurately to at least four significant figures, in a minimum amount of dilute HNO<sub>3</sub>. Add 10.0 mL concentrated HNO<sub>3</sub> and dilute to volume in a 1,000 mL volumetric flask with water.

5.4 Mixed calibration standard solutions - Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Table 3). Add 2 mL (1: 1) HNO<sub>3</sub> and 10 mL of (1: 1) HCl and dilute to 100 mL with water. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see Step 5.8) and monitored weekly for stability. Some typical calibration standard combinations are tested in Table 3. All mixtures should then be scanned using a sequential spectrometer to verify the absence of interelement spectral interference in the recommended mixed standard, solutions.

NOTE: addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

TABLE 3.  
MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
I I I	As, Mo
IV	Al, Ca, Cr, K, Na, Ni, Li, & Sr
V	Ag (see Note to Step 5.4), Mg, Sb, and Tl
VI	P

5.5 Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

5.5.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. Prepare a sufficient quantity to flush the system between standards and samples.

5.5.2 The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

5.6 The instrument check standard is prepared by the analyst by combining compatible elements at concentrations equivalent to the midpoint of their respective calibration curves (see Step 8.6.2.1 for use).

5.7 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the instrumental detection limits. In the absence of measurable analyte, overcorrection could go undetected & because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

5.5 Two types of blanks are required for the analysis. The calibration **blank** is used in establishing the analytical curve, and the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used **in** the sample processing.

5.5.1 The calibration blank is **prepared** by acidifying reagent water to the same **concentrations** of the acids found in the standards and samples. **Prepare** a sufficient quantity to flush the system **between** standards and **samples**.

5.5.2 The reagent blank must **contain** all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be **carried** through the complete procedure and contain the same acid concentration **in** the **final** solution as the sample solution **used** for analysis.

5.6 The instrument check standard is prepared by the analyst by combining compatible elements at concentrations equivalent to the midpoint of their respective calibration curves (see Step 8.6.2.1 for use).

5.7 The interference check solution is prepared to **contain known** concentrations of interfering elements that will provide **an** adequate test of the correction factors. Spike the sample with the elements of interest at approximate **concentrations** of 10 times the instrumental detection limits. In the absence of measurable **analyte**, over-correction could go undetected because a **negative** value would be reported as zero. If the particular instrument will display **overcorrection** as a negative number, this spiking procedure will not be **necessary**.

5.8 The quality **control** sample should be prepared in the same acid **matrix** as the calibration standards at 10 times the instrumental detection limits and **in** accordance with the instructions provided by the supplier.

## 6.0 SAMPLE COLLECTION, **PRESERVATION**, AND HANDLING

6.1 See the introductory material in Chapter **Three**, Metallic **Analytes**, Steps 3.1 through 3.3.

## 7.0 PROCEDURE

7.1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Water samples which have been **prefiltered** and acidified will not need acid digestion. **Solubilization** and digestion procedures are presented in Sample **Preparation Methods** (Methods **3005A3050A**).

7.2 Set up the instrument with proper operating parameters established **in** Step 4.2. The instrument must be allowed to become **thermally** stable before **beginning** (usually requiring at least 30 minutes of operation prior to calibration).

7.3 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the **typical** mixed **calibration** standard solutions described in Step 5.4. Flush the system with the calibration blank (Step 5.5.1) between each standard or as the **manufacturer** recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve should consist of a blank and three standards.

7.4 Before **beginning** the sample **run, reanalyze** the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5 % (or the established **control** limits, whichever **is** lower). If they do, follow the recommendations of the instrument manufacturer to **correct** for **this** condition.

7.5 Flush the system with the calibration-blank solution for at least **1 minute** (Step **5.5.1**) before the analysis of each sample (see Note to Step 7.3). Analyze the instrument check standard (Step 5.6) and the calibration blank (Step 5.5.1) after each 10 samples.

7.6 Calculations: If dilutions were performed, the **appropriate** factors must be applied to sample values. All results should be reported in **ug/L** with up to three significant figures.

## 8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection. All quality **control** measures described in Chapter One should be followed.

8.2 Dilute and **reanalyze** samples that are more **concentrated** than the linear **calibration** limit or use an alternate, less sensitive line for which quality control data is **already** established.

8.3 Employ a minimum of one reagent blank per sample batch to determine if contamination or any memory effects are occurring. A reagent blank is a volume of reagent water acidified with the same amounts of acids as were the standards and samples.

8.4 Analyze replicate samples at the frequency described in Chapter One. A replicate sample is a sample brought through the whole sample preparation and analytical process in duplicate.

8.5 It is recommended that whenever a new or unusual sample matrix is **encountered**, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in Steps 8.5.1 and 8.5.2, will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

8.5.1 Serial dilution: If the analyte **concentration** is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a **1:4** dilution should agree within  $\pm 10\%$  of the original determination. If not, a chemical or physical interference effect should be suspected.

8.5.2 **Matrix** spike addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within **75 %** to **125 %** of the known **value**. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be **suspected**.

**CAUTION:** If **spectral** overlap is **suspected**, use of computerized compensation, an alternate wavelength, or comparison with an alternate **method** is recommended.

8.6 Check the instrument standardization by analyzing appropriate check standards as follows.

8.6.1 Verify calibration every 10 samples and at the end of the analytical run, using a calibration blank (Step 5.5.1) and a check standard (Step 5.6).

8.6.1.1 The results of the check standard are to agree within 10% of the expected value; if not, terminate the analysis, **correct** the problem, and recalibrate the instrument.

8.6.1.2 The results of the calibration blank are to agree within three standard deviations of the mean blank value. If not, **repeat** the analysis two more times and average the results. If the average is not within **three** standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples.

8.6.2 Verify the interelement and **background** correction **factors** at the **beginning** and end of **an analytical** run or twice during every B-hour work **shift**, whichever is more **frequent**. Do this by analyzing the interference check sample (Step 5.7). Results should be within  $\pm 20\%$  of the true value **obtained in Step 8.6.1.1**.

8.6.3 Spiked replicate samples are to **be** analyzed at a frequency described in Chapter One.

8.6.3.1 The relative **percent** difference **between** replicate **determinations** is to be **calculated** as follows:

$$\text{RPD} = \frac{D1 - D2}{(D1 + D2)/2} \times 100$$

where:

RPD = relative percent difference.

**D<sup>1</sup>** = **first sample value**.

**D<sub>2</sub>** = second sample value (**replicate**).

(A control limit of + 20% RPD shall be used for sample **values** greater than ten times the instrument detection limit.)

8.6.3.2 The spiked replicate sample recovery is to be within + 20% of the actual value.

## 9.0 METHOD PERFORMANCE

9.1 In an EPA **round-robin** Phase 1 study, seven laboratories applied the ICP technique to acid distilled water **matrices** that had been spiked with various metal concentrates. Table 4 lists the true values, the **mean reported** values, and the mean percent relative standard deviations\*

9.2 In a single **laboratory** evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was  $9 \pm 2\%$ . The mean percent recovery of spiked elements for all wastes was  $93 \pm 6\%$ . Spike levels ranged from **100 ug/L** to **100 mg/L**. The wastes included sludges and industrial wastewaters.

#### 10.0 REFERENCES

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TABLE 4.  
ICP PRECISION AND ACCURACY DATA=

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True Value (ug/L)	Mean Reported Value (ug/L)	Mean <sup>b</sup> SD (%)	True Value (ug/L)	Mean Reported Value (ug/L)	Mean <sup>b</sup> SD (%)	True Value (ug/L)	Mean Reported Value (ug/L)	Mean <sup>b</sup> SD (%)
Be	750	733	6.2						5.2
Mn	350	345	2.7	15	15	9.8 6.7	180 100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	5.1	10	10	18	50	50	3.3
Fe	250	235	3.0	11	11	40	70	67	7.9
Al	600 700	696 594	5.6	60	62	33	180	178	6.0
Cd	50	48		20	20	14	13	16	13
Co	700	512	5.8 .5	30.9	28.1	120	160	55	
Ni	250	245	16 24	30	32	11	80	14	14
Pb	250	236							
Zn	200	201	5.6			80			
Se <sup>c</sup>	40	32	21.9	16 6	19 8.5	45 42	80 10	82 8.5	9.4 8.3

<sup>a</sup>Not all elements were analyzed by all laboratories.

<sup>b</sup>SD = standard deviation.

<sup>c</sup>Results for Se are from two laboratories.

METHOD 6010A  
INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY



