METHOD 29 COMPARISON TESTING OF AN X-RAY BASED CONTINUOUS EMISSION MONITOR AT TOOELE ARMY DEPOT

Contract No. DACA42-02-P-0072
(TASK 6)

FINAL REPORT

Prepared for

U. S. Army Corps of Engineers
Engineer Research and Development Center
Construction Engineering Research Laboratory

Submitted By

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July 31, 2002

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EXECUTIVE SUMMARY

Cooper Environmental Services (CES) has developed an on-line multi-metal **X**-ray based **C**ontinuous **E**mission **M**onitor (XCEM) capable of simultaneously measuring 19 elements in stack gas emissions every 20 minutes. The U.S. Army purchased an XCEM for monitoring emissions at its demunitions incinerator APE-1236 on the Tooele Army Depot (TEAD). In order to validate the XCEM, a series of 12 comparison tests with EPA's Method 29 (M29) were conducted while the stack was being spiked by MSE-TA of Butte, MT. Results were compared to criteria found in EPA's proposed performance specification 10 for multi-metal continuous emission monitors (PS10).

During the testing, the XCEM had an "uptime" of better than 98%, met all quality assurance parameters, and had a precision that was better than M29. The XCEM also showed good correlation with Method 29 for elements that had significant variability in concentration during testing (Table ES1).

APE-1236 emissions have the potential to approach state-mandated emission limits for three elements: Pb, Cd, and Cr. The XCEM met the PS10 20% relative accuracy criteria for all three of these elements with RA's of 4%, 17%, and 15% respectively. XCEM data was also compared to M29 data for five elements that are typically found in concentrations well below the site emission limits: As, Hg, Sb, Ni, and Ba. A final non-regulated element, Zn, was also spiked by MSE-TA and examined during validation testing. The XCEM met the RA criteria for two of the non-limiting elements Ba (4%) and Sb (20%), but was uniformly high relative to M29 for As, Ni, Zn, and Hg.

An error analysis was conducted to determine the source of the difference between M29 and the XCEM. Calibration errors and spectral interferences were checked by reevaluating the XCEM filter with CES's QuanX and submitting filter samples to an independent laboratory for analysis. The results indicate that, for As, Ni, and Zn, the XCEM calibration was not the primary source of error. Aside from calibration and spectral errors, other potential sources of error for the XCEM include loss during transport, low filter trapping efficiency, deposit positioning errors, and incorrect flow measurements. Each of these error sources is highly unlikely. The first three sources of error would only result in XCEM concentrations lower than M29. An incorrect flow measurement would have resulted in all metals being uniformly high or low since one XCEM flow measurement is applied to all of the metals for each run. For this reason, the differences in concentration for As, Ni, and Zn appear to be due to M29 analytical errors.

An analysis of Hg on the XCEM filter determined that particulate phase Hg was being vaporized over time. A comparison of XCEM spectra generated during the test with reanalysis six weeks later showed a loss of 30% of the Hg from the XCEM filter. M29 particulate concentrations on the M29 filters were 15 to 30 times higher than typical and were highly correlated with differences between the XCEM and M29. The filters, which were not cooled while being shipped to the M29 laboratory, could have lost the Hg prior to analysis.

Following the conclusion of the M29 tests, the XCEM was used in a series of diagnostic tests to evaluate air pollution control technology installed at APE-1236. Using the XCEM, TEAD personnel developed baseline data for lead and zinc during incineration of various munitions. Next, a bypass duct was blocked with a metal plate resulting in a greater than 90% drop in metal concentrations. Using this data, TEAD was better able to understand sources of Pb in the emissions.

Currently, the XCEM is being moved to a newly developed test furnace at TEAD. The furnace, operated by the Ammunition Equipment Division, anticipates using the instrument to rapidly determine effects of changes in munitions or control strategies.

The continued use of the XCEM to diagnose and assist with process control indicates the value of having an installed continuous emission monitor for multi-metals at TEAD. CES recommends the adoption of the XCEM as a validated monitor for incinerators such as APE-1236. Recent advances in XRF technology have allowed for a miniaturized version of the XCEM with better detection limits than the current system. CES also recommends that this technology be incorporated into a mobile version of the XCEM for the army's stack testing organization (CHPPM) and an extension of the technology to a mercury-dedicated XCEM.

Table ES1. Relative Accuracy and Correlation

Elem.	Avg. M29 Conc. (µg/m³)	Avg. XC Conc. (µg/m³)	Avg. Pred. Conc. (µg/m³)	Concentrations potentially approach site limit.	RA %	Corr. Coeff. (Runs 3-13)	Notes
Pb	101	101	107	Yes	**4**	0.98	**Met PS10 RA criteria.**
Cd	42.0	31.5	36.4	Yes	**17**	NA	**Met PS10 RA criteria.**
Cr	4.9	5.4	4.7	Yes	**15**	0.64	**Met PS10 RA criteria.**
As	11.1	13.8	15.2	No	27	0.85	XCEM uniformly higher than M29 by 24%.
Hg	305	385	326	No	33	NA	Met criteria for runs 1-5. XCEM higher for runs 6-12. Difference likely due to loss from M29 filter.
Sb	164	192	194	No	**20**	NA	**Met PS10 RA criteria.**
Ni	218	281	268	No	33	NA	XCEM uniformly higher than M29 by 30%.
Ba	216	216	226	No	**4**	NA	**Met PS10 RA criteria.**
Zn	202	290	288	NR	43	NA	XCEM uniformly higher than M29 by 42%.

NR: Not regulated
NA: Correlation coefficient not available since element was only spiked at one level.

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LIST OF ABBREVIATIONS

AMS	Advanced Monitoring Systems; part of the ETV program
APE	Ammunition Peculiar Equipment
As	Arsenic
Ba	Barium
Cd	Cadmium
CEM	Continuous Emissions Monitor
CES	Cooper Environmental Services of Beaverton, OR
CHPPM	Center for Health Promotion and Preventative Maintenance
Cr	Chromium
DLS	Director of Laboratory Services
DSLP	Dry Standard Liters Per Minute
DSCM	Dry Standard Cubic Meters
EPA	United States Environmental Protection Agency
ETV	Environmental Technology Verification program
Hg	Mercury
HVM	High Volatile Metals (mercury)
LVM	Low Volatile Metals (cadmium, lead)
M29	EPA standard method 29
M301	EPA standard method 301
MACT	Maximum Achievable Control Technology
MFC	Mass Flow Controller
MFM	Mass Flow Meter
MM-CEM	Multi-metal Continuous Emission Monitor
MSE-TA	MSE-Technology Applications Inc. of Butte, MT.
Ni	Nickel
Pb	Lead
PLC	Programmable Logic Circuit
PS10	EPA's proposed Performance Specification 10 for multi-metal CEMS
QA	Quality Assurance
QC	Quality Control
QN	QuanX XRF located at CES
RA	Relative Accuracy
RSD	Relative Standard Deviation (% RSD equals precision)
Sb	Antimony
SVM	Semi-volatile metals (arsenic, beryllium, chromium)
TEAD	Tooele Army Depot
USACERL	U.S. Army Construction Engineering Research Library
XCEM	X-ray based Continuous Emission Monitor
XRF	X-Ray Fluorescence
Zn	Zinc
µg/DSCM	Micro-grams per dry standard cubic meter

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1.0 INTRODUCTION

Cooper Environmental Services (CES) has developed an X-ray based multi-metals Continuous Emissions Monitor (XCEM) capable of providing near real-time data for up to 19 elements found in smoke stack emissions. During the spring of 2001, the XCEM was installed at the Tooele Army Depot (TEAD) munitions incinerator. Following installation, a series of comparison tests to EPA's Method 29 (M29) were conducted with the XCEM during May 2001 (Bryson, 2001, Johnsen, 2001). Although no final performance specifications exist for multi-metal CEMs, the results of these tests were compared to EPA's draft Performance Specification 10 (PS10). The XCEM met the precision, quality assurance, response time, and response to change in concentration criteria of PS10, but only met relative accuracy criteria for three elements (chromium, cadmium, and nickel). An evaluation of the test parameters indicated that changes to the transport line, improvements in calibration, and testing of the XCEM vs. stack spiking would improve the XCEM relative accuracy.

During the spring of 2002, improvements were made to the XCEM transport line and a second series of preliminary tests were conducted to better understand calibration and stack spiking efficiency. Finally, in May 2002 a series of Method 29 tests were conducted to evaluate the measurement capabilities of the upgraded XCEM. This report discusses the XCEM results relative to the Method 29 testing. A second companion report (Johnsen, 2002) discusses the results of the transport line changes and preliminary tests prior to Method 29.

2.0 RESULTS

2.1 METHOD 29 CONCENTRATIONS

Method 29 (M29) tests were conducted using duplicate sample trains located at the same stack height as the XCEM probe. In general, the two trains were in good agreement (Pattison, 2002a). More than 90% of the paired M29 concentrations were within 10% of each other. Of the eleven reported concentrations that were not within 10%, nine were measurements of Sn. Since M29 has not been approved for Sn (EPA, 1992), CHPPM determined that the M29 Sn values were not valid.

Overall, train A was higher than train B by about 3% with about 78% of the concentrations in train A being higher than their train B counterpart. An average of trains A and B was used for comparison to the XCEM reported concentrations.

M29 data used for comparison to the XCEM is the same as reported in the M29 report (Pattison, 2002a) with the exception of a one to three percent correction compensating for the laboratory's inadvertent subtraction of an estimated blank concentration when the blank concentrations were below the method reporting limit (Severen-Trent, 2002).

Table 1. Method 29 Concentrations (µg/DSCM)

RUN	Pb			Cd			Cr			As			Hg			Sb		
	A	B	AVG	A	B	AVG	A	B	AVG	A	B	AVG	A	B	AVG	A	B	AVG
1	74	71	73	31	28	29	3.5	3.6	3.6	8.1	7.4	7.8	344	320	332	154	148	151
2	75	78	77	32	32	32	4.0	4.1	4.0	8.4	8.0	8.2	337	331	334	188	176	182
3	99	96	98	36	34	35	6.7	6.2	6.4	11.7	11.2	11.4	306	283	294	187	180	183
4	37	39	38	31	31	31	4.8	5.2	5.0	11.5	12.1	11.8	347	307	327	168	164	166
5	29	26	28	32	30	31	5.3	5.2	5.2	12.3	11.1	11.7	319	317	318	172	163	168
6	148	146	147	32	31	31	5.0	4.7	4.8	11.6	10.9	11.2	291	269	280	160	163	162
7	138	132	135	32	31	32	5.0	4.8	4.9	11.8	11.4	11.6	279	291	285	169	159	164
8	131	126	128	33	32	32	5.2	4.9	5.1	12.6	11.8	12.2	309	303	306	165	158	162
9	121	122	122	32	32	32	4.9	5.4	5.2	12.0	12.2	12.1	312	305	309	153	161	157
10	140	129	135	31	29	30	5.0	4.8	4.9	11.3	10.8	11.0	294	289	292	164	151	157
11	119	118	119	32	31	31	4.9	4.7	4.8	11.7	11.5	11.6	297	293	295	162	164	163
12	114	111	113	31	31	31	4.8	4.8	4.8	11.9	11.7	11.8	308	278	293	154	154	154

RUN	Ni			Ba			Zn			Sn		
	A	B	AVG	A	B	AVG	A	B	AVG	A	B	AVG
1	209	191	200	222	206	214	203	186	195	132	144	138
2	235	235	235	249	248	248	216	208	212	131	168	149
3	240	228	234	252	243	247	222	208	215	207	199	203
4	207	220	213	195	211	203	192	201	196	66	90	78
5	227	235	231	215	198	207	202	191	196	57	69	63
6	236	214	225	217	215	216	218	200	209	131	108	120
7	230	205	218	220	204	212	206	198	202	60	74	67
8	224	213	219	214	206	210	211	196	204	47	48	47
9	222	221	221	204	209	206	204	200	202	41	35	38
10	219	192	205	218	199	208	205	192	199	88	64	76
11	218	214	216	210	210	210	205	201	203	44	36	40
12	202	195	199	208	201	204	199	192	196	31	25	28

2.2 PREDICTED STACK GAS CONCENTRATIONS

Predicted stack gas concentrations were determined by adding the MSE-TA calculated spiked concentrations with background concentrations based on XCEM measurements when munitions were being burned but no spiking was occurring. The background was essentially zero for five elements: Cr, As, Hg, Sb, and Ni. For Cd, Ba, and Zn, the background correction was small relative to the MSE-TA spiked concentration -- 17%, 15%, and 8% respectively. However, for Pb, the background accounted for 100% of the Pb in runs 1-5 and 35% of the Pb in runs 6 through 12.

2.2.1 MSE-TA Spike Injection

During M29 testing, MSE-TA spiked known masses of Pb, Cd, Cr, As, Hg, Sb, Ni, Ba, and Zn into the stack (Bryson, 2002). These spiked masses were divided by the stack flow to obtain concentrations in micrograms per dry standard cubic meter (µg/DSCM). MSE-TA mass concentrations in solution were cross-checked by submitting aliquots from M29 runs 5 and 6 to

an independent laboratory for analysis (HKM labs, Butte, MT). HKM's results were within 7% of MSE-TA's estimates for all elements except As which was 23% lower according to HKM labs than reported by MSE-TA. Because of the limited HKM data, no adjustments were made to MSE-TA reported data. The potential impact of the As difference is discussed in Section 3.0 and in a report by Cooper et. al. (Cooper, 2002).

Measurements of stack flow by CHPPM were crosschecked with the stack continuous velocity monitor for accuracy and were found to be within 6% of each other (Table 2). The CHPPM flows were determined using a velocity traverse at the same stack height as the XCEM probe and are believed to be more representative of true flows than the continuous velocity monitor (Pattison, 2002b). For this reason, the CHPPM flows were used to calculate the predicted concentrations.

Table 2. APE-1236 Stack Flow Rates During M29 Testing

RUN	TEAD	M29A	M29B	M29	TEAD/ M29
	DSCM/ HR	DSCM/ HR	DSCM/ HR	DSCM/ HR	%
1	5,173	4,718	4,659	4,689	110
2	5,037	4,638	4,652	4,645	108
3	4,998	4,527	4,532	4,530	110
4	4,889	4,680	4,688	4,684	104
5	4,838	4,672	4,688	4,680	103
6	4,970	4,578	4,580	4,579	109
7	4,826	4,607	4,613	4,610	105
8	4,785	4,641	4,647	4,644	103
9	4,676	4,662	4,672	4,667	100
10	5,060	4,589	4,600	4,594	110
11	4,960	4,593	4,662	4,628	107
12	4,879	4,660	4,670	4,665	105
AVG.	4,924	4,630	4,639	4,635	106

2.2.2 Background Metal Concentration

TEAD incinerated 20 mm TPM55A2 bullets during all twelve M29 runs. This ammo, which is used for target training, does not contain significant quantities of hazardous elements. However, measurable residual concentrations of Pb, Cd, Ba, Zn, and Sn were found in the stack gas from earlier incineration of other munitions. Table 3 shows XCEM results for elements measured on May 13th and May 15th while the 20 mm bullets were being burned and MSE-TA was not spiking into the stack. The May 13th metal concentrations were significantly higher than the May15th concentrations. This is consistent with incineration of relatively clean munitions scouring the stack. Background concentrations for Cr, As, Hg, Ni, and Sb were below XCEM detection limits and were reported as 0 µg/DSCM.

Table 3. APE1236 Stack Concentrations With Munitions Incineration But No Spiking (µg/DSCM)

Date	Run	PB	CD	BA	ZN	SN
5/13/02	899	94.5	11.5	68.7	38.3	487
5/13/02	900	85.9	5.9	64.8	42.7	604
5/13/02	901	78.2	8.4	43.6	39.3	466
5/13/02	902	60.0	9.9	20.1	22.9	227
5/13/02	903	68.2	10.0	74.5	26.5	272
5/13/02	904	53.3	12.2	41.1	39.3	282
5/13/02	905	53.8	6.4	10.6	40.3	231
5/13/02	906	44.7	8.0	18.1	21.2	205
5/13/02	907	54.7	6.0	22.3	23.9	275
5/13/02	908	44.5	5.7	49.3	22.6	259
AVG.		**63.8**	**8.4**	**41.3**	**31.7**	**331**
5/15/02	990	22.3	0.6	12.6	8.4	120
5/15/02	991	25.0	4.9	29.4	8.8	135
5/15/02	992	21.4	1.3	5.6	6.7	114
5/15/02	993	8.9	0.1	29.4	2.9	38
AVG.		**19.4**	**1.7**	**19.3**	**6.7**	**102**

2.2.3 Use of Sn as a Surrogate for Background Metals

Figure 1 shows the relationship between Pb, Ba, Zn, and Sn when spiking was not occurring. The correlations indicate that Pb, Ba, Zn and Sn background concentrations stem from the same source. Since Sn was not spiked by MSE-TA, its concentration was used as an indicator of the background during spiking periods. The background contribution of the other elements was estimated by their relationship to Sn according to the equations in Figure 1. Figure 2 shows the XCEM measurements of Sn during M29 testing. A surge in Sn concentrations is observed each morning after the bypass damper is opened. The surge is followed by a gradual decrease in Sn concentrations throughout the day. Although Cd was not found in high enough concentrations to certify its relationship with Sn, it was assumed to behave in the same manner as the other metals. Combining the MSE-TA spike injection estimates with the estimated background concentrations resulted in predicted concentrations as shown in Table 3.

Figure 1. Correlation Between Sn and Other APE1236 Metals With Munitions Burning and No Spiking

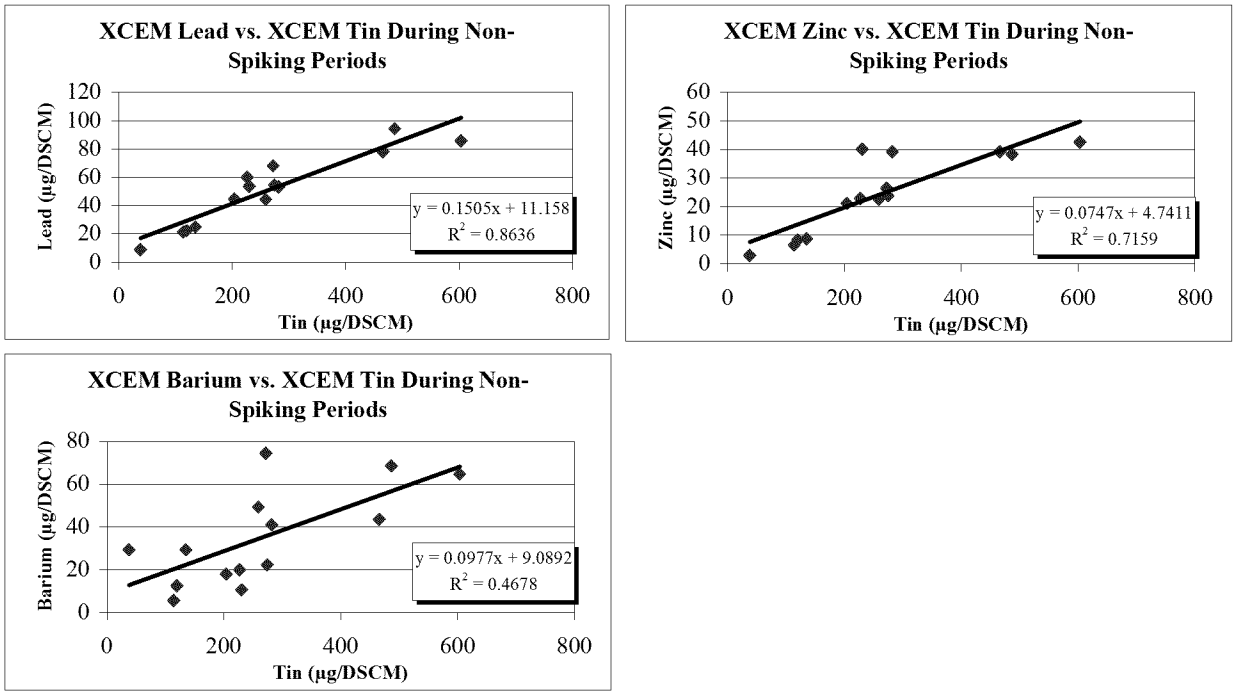
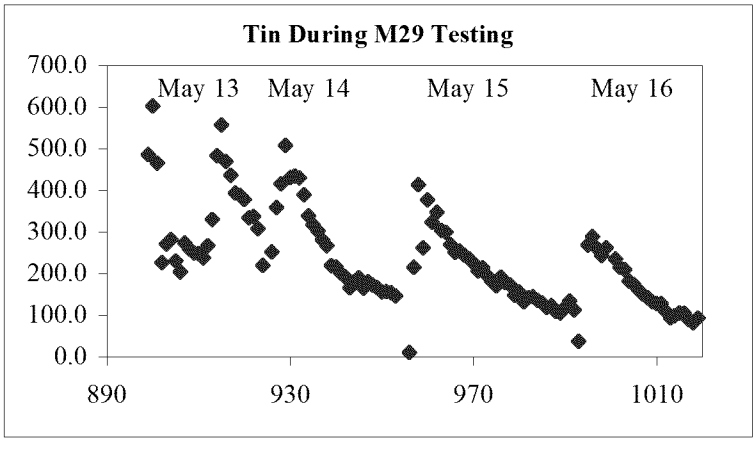


Figure 2. XCEM Tin Measurements During M29 Testing



2.3 XCEM CONCENTRATION DETERMINATION

XCEM concentrations were determined every 20 minutes for Pb, Cd, Cr, As, Ni, Hg, Ba, Sb, Zn, and Sn (Table 5). A Pd rod is permanently mounted in the XRF detection area and is measured with every sample. The consistency of the Pd concentrations provides quality assurance of the instruments stability During M29 testing, the XCEM successfully carried out 120 runs with only two runs falling outside of the Pd quality assurance criteria due to air conditioning problems. This represents an uptime of 98%.

Table 4. Predicted Stack Concentrations Based on MSE-TA Spiking and Background Estimates (µg/DSCM)

RUN	CHROMIUM			CADMIUM			LEAD			ARSENIC			NICKEL		
	MSE	BKG	PRD	MSE	BKG	PRD	MSE	BKG	PRD	MSE	BKG	PRD	MSE	BKG	PRD
1	2.9	0.0	2.9	32.0	9.4	41.5	0.0	67	67	10.6	0.0	10.6	267	0.0	267
2	2.9	0.0	2.9	31.5	8.4	39.8	0.0	61	61	10.7	0.0	10.7	268	0.0	268
3	5.2	0.0	5.2	37.5	11.1	48.6	0.0	77	77	16.7	0.0	16.7	275	0.0	275
4	5.0	0.0	5.0	36.5	5.0	41.6	0.0	41	41	16.1	0.0	16.1	265	0.0	265
5	5.0	0.0	5.0	37.2	4.1	41.4	0.0	36	36	16.1	0.0	16.1	266	0.0	266
6	5.0	0.0	5.0	36.9	8.5	45.4	105	61	167	16.0	0.0	16.0	271	0.0	271
7	5.1	0.0	5.1	37.7	6.0	43.7	104	46	150	16.4	0.0	16.4	269	0.0	269
8	5.1	0.0	5.1	37.1	4.4	41.5	103	37	140	16.2	0.0	16.2	267	0.0	267
9	5.1	0.0	5.1	37.1	3.4	40.5	103	31	134	16.2	0.0	16.2	266	0.0	266
10	4.8	0.0	4.8	35.3	5.9	41.1	105	46	151	15.2	0.0	15.2	270	0.0	270
11	5.0	0.0	5.0	36.5	3.5	39.9	104	32	136	16.0	0.0	16.0	268	0.0	268
12	5.1	0.0	5.1	36.6	2.4	39.0	103	26	128	16.2	0.0	16.2	266	0.0	266
AVG.	**4.7**	**0.0**	**4.7**	**36.0**	**6.0**	**42.0**	**61**	**47**	**107**	**15.2**	**0.0**	**15.2**	**268**	**0.0**	**268**
SD	**0.8**	**0.0**	**0.8**	**2.1**	**2.7**	**2.7**	**53**	**16**	**47**	**2.2**	**0.0**	**2.2**	**2.8**	**0.0**	**2.8**

RUN	MERCURY			BARIUM			ANTIMONY			ZINC		
	MSE	BKG	PRD	MSE	BKG	PRD	MSE	BKG	PRD	MSE	BKG	PRD
1	324	0.0	324	192	45.3	237	192	0.0	192	267	32.5	300
2	325	0.0	325	196	41.2	238	196	0.0	196	268	29.3	297
3	333	0.0	333	201	51.6	253	201	0.0	201	275	37.3	312
4	322	0.0	322	194	28.3	223	194	0.0	194	265	19.5	285
5	323	0.0	323	193	25.0	218	193	0.0	193	266	16.9	283
6	329	0.0	329	199	41.6	240	199	0.0	199	271	29.6	301
7	327	0.0	327	197	31.9	229	197	0.0	197	269	22.2	291
8	325	0.0	325	192	25.9	218	192	0.0	192	267	17.6	285
9	324	0.0	324	189	22.1	212	189	0.0	189	266	14.7	280
10	328	0.0	328	194	31.6	226	194	0.0	194	270	22.0	292
11	326	0.0	326	193	22.5	215	193	0.0	193	268	15.0	283
12	322	0.0	322	190	18.4	209	190	0.0	190	266	11.9	278
AVG.	**326**	**0.0**	**326**	**194**	**32.1**	**226**	**194**	**0.0**	**194**	**268**	**22.4**	**290**
SD	**3.3**	**0.0**	**3.3**	**3.4**	**11**	**13**	**3.4**	**0**	**3**	**2.8**	**8**	**10**

Table 5. XCEM Concentrations (µg/DSCM)

Date	START	STOP	XC RUN	M29 RUN	XCEM CONC. (µg/DSCM)										CES CONC. (µg/DSCM)									
					AS	BA	CD	CR	HG	NI	PB	SB	SN	ZN	AS	BA	CD	CR	HG	NI	PB	SB	SN	ZN
5/13	7:57 AM	8:17 AM	899		0.0	69	11.5	1.2	2	1	95	0	487	38										
5/13	8:17 AM	8:37 AM	900		0.4	65	5.9	0.6	1	0	86	0	604	43										
5/13	8:37 AM	8:57 AM	901		0.2	44	8.4	0.3	2	1	78	1	466	39										
5/13	8:57 AM	9:17 AM	902		2.1	20	9.9	0.8	1	0	60	3	227	23										
5/13	9:18 AM	9:37 AM	903		0.0	75	10.0	1.3	0	0	68	5	272	27										
5/13	9:37 AM	9:57 AM	904		2.2	41	12.2	0.9	1	2	53	1	282	39										
5/13	9:57 AM	10:17 AM	905		0.0	11	6.4	0.7	1	0	54	5	231	40										
5/13	10:17 AM	10:37 AM	906		1.3	18	8.0	0.3	1	0	45	3	205	21										
5/13	10:37 AM	10:57 AM	907		0.0	22	6.0	0.6	1	1	55	5	275	24										
5/13	10:57 AM	11:17 AM	908		1.4	49	5.7	0.4	1	1	45	3	259	23										
5/13	11:17 AM	11:36 AM	909		8.5	129	26.4	3.4	218	200	44	106	250	210										
5/13	**11:37 AM**	**11:57 AM**	**910**	**1**	**8.0**	**242**	**30.8**	**2.9**	**347**	**254**	**48**	**187**	**249**	**269**	**8.6**	**210**	**27.5**	**3.2**	**261**	**270**	**51**	**172**	**226**	**296**
5/13	**11:57 AM**	**12:17 PM**	**911**	**1**	**10.1**	**202**	**33.2**	**3.2**	**360**	**257**	**46**	**170**	**238**	**273**	**10.8**	**188**	**28.0**	**2.6**	**264**	**268**	**46**	**176**	**224**	**295**
5/13	**12:18 PM**	**12:38 PM**	**912**	**1**	**9.1**	**222**	**35.0**	**3.7**	**365**	**273**	**47**	**184**	**268**	**283**	**9.5**	**222**	**31.9**	**3.6**	**269**	**277**	**57**	**172**	**271**	**306**
5/13	**12:38 PM**	**12:59 PM**	**913**	**1**	**8.1**	**215**	**32.0**	**4.1**	**356**	**264**	**59**	**192**	**331**	**279**	**9.0**	**210**	**29.5**	**3.8**	**244**	**247**	**63**	**161**	**318**	**276**
5/13	**12:59 PM**	**1:19 PM**	**914**	**1**	**11.5**	**223**	**40.4**	**3.7**	**385**	**278**	**87**	**182**	**484**	**301**	**8.5**	**206**	**29.9**	**3.1**	**263**	**262**	**84**	**159**	**399**	**297**
5/13	**1:19 PM**	**1:40 PM**	**915**	**1**	**10.9**	**265**	**37.4**	**3.8**	**371**	**279**	**94**	**190**	**558**	**303**	**8.6**	**193**	**27.5**	**3.0**	**244**	**248**	**88**	**161**	**460**	**286**
5/13	**1:40 PM**	**2:01 PM**	**916**	**1**	**12.6**	**256**	**34.1**	**3.7**	**371**	**280**	**83**	**181**	**471**	**302**	**11.3**	**208**	**29.5**	**2.8**	**260**	**276**	**83**	**170**	**411**	**312**
5/13	2:01 PM	2:22 PM	917		9.2	241	36.9	3.5	387	285	79	191	437	313	9.4	229	29.3	3.0	264	284	79	174	374	321
5/13	2:22 PM	2:47 PM	918		10.2	240	35.0	3.2	366	275	77	192	394	297	10.4	231	30.0	3.3	278	293	80	183	353	325
5/13	**2:47 PM**	**3:08 PM**	**919**	**2**	**9.6**	**272**	**34.3**	**3.7**	**381**	**278**	**76**	**206**	**389**	**295**	**10.3**	**247**	**28.8**	**3.1**	**268**	**273**	**75**	**173**	**341**	**301**
5/13	**3:08 PM**	**3:29 PM**	**920**	**2**	**7.1**	**241**	**37.5**	**4.8**	**394**	**281**	**77**	**191**	**379**	**300**	**10.4**	**209**	**28.4**	**3.2**	**258**	**275**	**69**	**182**	**316**	**303**
5/13	**3:29 PM**	**3:50 PM**	**921**	**2**	**11.0**	**233**	**39.0**	**3.7**	**380**	**290**	**72**	**206**	**335**	**302**	**10.4**	**231**	**33.0**	**3.4**	**264**	**288**	**71**	**183**	**306**	**314**
5/13	**3:50 PM**	**4:10 PM**	**922**	**2**	**8.7**	**255**	**32.0**	**3.8**	**390**	**294**	**67**	**206**	**338**	**308**	**9.4**	**209**	**26.5**	**3.0**	**230**	**257**	**61**	**171**	**275**	**281**
5/13	**4:11 PM**	**4:31 PM**	**923**	**2**	**10.5**	**231**	**38.0**	**3.9**	**374**	**278**	**59**	**196**	**309**	**291**	**10.2**	**207**	**29.3**	**3.1**	**240**	**275**	**58**	**172**	**261**	**301**
5/13	**4:31 PM**	**4:52 PM**	**924**	**2**	**9.1**	**230**	**33.3**	**4.4**	**360**	**273**	**47**	**191**	**221**	**280**	**11.0**	**228**	**30.9**	**3.5**	**245**	**292**	**49**	**187**	**198**	**318**
5/14	7:04 AM	7:25 AM	926		6.8	136	20.6	3.4	148	142	50	102	253	158	8.3	117	18.0	3.0	93	150	52	87	227	173
5/14	7:25 AM	7:45 AM	927		13.8	201	42.8	5.6	309	243	79	178	359	283	14.6	211	35.8	4.7	222	260	76	160	314	297
5/14	**7:45 AM**	**8:06 AM**	**928**	**3**	**13.6**	**210**	**38.6**	**6.1**	**350**	**259**	**84**	**185**	**417**	**290**	**12.8**	**173**	**31.7**	**4.7**	**253**	**267**	**81**	**145**	**369**	**311**
5/14	**8:06 AM**	**8:26 AM**	**929**	**3**	**14.8**	**216**	**39.7**	**6.2**	**353**	**265**	**95**	**189**	**508**	**294**	**13.2**	**182**	**33.1**	**5.2**	**247**	**256**	**96**	**156**	**443**	**300**
5/14	**8:27 AM**	**8:47 AM**	**930**	**3**	**14.5**	**229**	**34.7**	**5.1**	**354**	**250**	**80**	**187**	**431**	**277**	**13.6**	**207**	**30.0**	**4.3**	**254**	**250**	**78**	**153**	**378**	**283**
5/14	**8:47 AM**	**9:08 AM**	**931**	**3**	**10.5**	**218**	**36.7**	**5.5**	**347**	**245**	**78**	**175**	**435**	**269**	**14.2**	**212**	**32.0**	**4.9**	**283**	**280**	**87**	**156**	**407**	**318**
5/14	**9:08 AM**	**9:29 AM**	**932**	**3**	**12.2**	**275**	**37.0**	**6.2**	**380**	**266**	**81**	**193**	**431**	**292**	**13.3**	**199**	**31.5**	**4.9**	**271**	**259**	**78**	**168**	**373**	**293**
5/14	**9:29 AM**	**9:49 AM**	**933**	**3**	**16.7**	**218**	**36.9**	**5.6**	**399**	**286**	**69**	**207**	**391**	**302**										

Table 5. XCEM Concentrations (µg/DSCM) (Cont.)

Date	START	STOP	XC RUN	M29 RUN	XCEM CONC. (µg/DSCM)										CES CONC. (µg/DSCM)									
					AS	BA	CD	CR	HG	NI	PB	SB	SN	ZN	AS	BA	CD	CR	HG	NI	PB	SB	SN	ZN
5/14	9:49 AM	10:10 AM	934		15.7	99	35.6	6.4	391	278	60	63	340	294										
5/14	10:10 AM	10:31 AM	935		13.2	58	36.2	5.8	356	261	61	45	317	278										
5/14	10:31 AM	10:51 AM	936		15.5	170	40.0	5.4	354	258	51	161	304	275										
5/14	10:51 AM	11:12 AM	937		15.0	21	38.2	6.2	373	275	47	12	282	287										
5/14	11:12 AM	11:32 AM	938		14.6	182	36.0	5.6	373	277	46	181	268	287										
5/14	**11:32 AM**	**11:53 AM**	**939**	**4**	**14.8**	**213**	**37.4**	**5.3**	**360**	**265**	**40**	**181**	**220**	**273**	**14.3**	**179**	**30.5**	**4.8**	**301**	**274**	**43**	**172**	**203**	**294**
5/14	**11:53 AM**	**12:13 PM**	**940**	**4**	**12.7**	**208**	**38.7**	**6.1**	**362**	**262**	**43**	**198**	**216**	**268**	**14.3**	**190**	**32.2**	**5.1**	**319**	**299**	**43**	**175**	**203**	**320**
5/14	**12:13 PM**	**12:34 PM**	**941**	**4**	**14.2**	**197**	**34.1**	**4.9**	**353**	**256**	**36**	**188**	**203**	**266**	**14.5**	**213**	**31.6**	**5.1**	**304**	**284**	**42**	**170**	**193**	**302**
5/14	**12:34 PM**	**12:54 PM**	**942**	**4**	**12.4**	**224**	**37.1**	**5.9**	**380**	**280**	**36**	**187**	**194**	**285**	**13.7**	**205**	**32.7**	**5.2**	**305**	**285**	**39**	**179**	**179**	**305**
5/14	**12:54 PM**	**1:15 PM**	**943**	**4**	**16.1**	**207**	**39.7**	**6.0**	**376**	**278**	**33**	**189**	**167**	**280**	**14.8**	**215**	**33.3**	**5.4**	**286**	**275**	**33**	**177**	**164**	**291**
5/14	**1:15 PM**	**1:35 PM**	**944**	**4**	**15.6**	**209**	**38.9**	**6.6**	**376**	**276**	**29**	**193**	**182**	**282**	**15.5**	**204**	**34.7**	**5.0**	**292**	**291**	**34**	**182**	**165**	**306**
5/14	1:35 PM	1:56 PM	945		13.5	183	32.6	5.0	368	273	29	170	191	275	14.4	198	33.3	5.4	312	281	30	163	165	299
5/14	1:56 PM	2:16 PM	946		14.8	33	36.3	6.6	363	268	27	13	165	273	14.0	40	30.3	5.2	291	282	30	10	157	302
5/14	**2:16 PM**	**2:37 PM**	**947**	**5**	**14.1**	**225**	**41.3**	**5.1**	**369**	**269**	**29**	**196**	**181**	**274**	**14.4**	**198**	**30.0**	**5.2**	**331**	**283**	**30**	**178**	**154**	**299**
5/14	**2:37 PM**	**2:57 PM**	**948**	**5**	**17.1**	**207**	**35.5**	**6.2**	**387**	**282**	**26**	**190**	**173**	**286**	**14.9**	**190**	**28.0**	**5.1**	**309**	**266**	**27**	**169**	**149**	**283**
5/14	**2:57 PM**	**3:18 PM**	**949**	**5**	**14.7**	**235**	**41.7**	**6.9**	**390**	**281**	**29**	**190**	**167**	**281**	**13.7**	**197**	**30.4**	**4.7**	**300**	**255**	**26**	**164**	**137**	**271**
5/14	**3:18 PM**	**3:38 PM**	**950**	**5**	**16.1**	**220**	**30.6**	**5.8**	**378**	**275**	**25**	**195**	**157**	**273**	**14.1**	**200**	**28.2**	**5.1**	**311**	**269**	**26**	**166**	**143**	**286**
5/14	**3:38 PM**	**3:59 PM**	**951**	**5**	**15.9**	**222**	**36.8**	**5.9**	**374**	**268**	**22**	**196**	**157**	**271**	**12.8**	**186**	**31.7**	**4.1**	**288**	**242**	**24**	**166**	**129**	**257**
5/14	**3:59 PM**	**4:19 PM**	**952**	**5**	**13.9**	**258**	**35.3**	**6.3**	**374**	**271**	**26**	**202**	**155**	**276**	**14.2**	**190**	**29.7**	**5.7**	**309**	**281**	**25**	**184**	**133**	**295**
5/14	**4:20 PM**	**4:40 PM**	**953**	**5**	**14.1**	**228**	**40.7**	**6.2**	**395**	**286**	**26**	**209**	**147**	**287**	**16.0**	**217**	**35.3**	**5.7**	**346**	**300**	**27**	**196**	**142**	**319**
5/15	6:57 AM	7:18 AM	956		5.6	70	20.5	3.1	148	138	53	70	12	138										
5/15	7:18 AM	7:38 AM	957		11.0	191	41.3	5.8	341	273	139	191	216	275	14.0	176	27.5	5.2	286	276	138	154	185	298
5/15	**7:38 AM**	**7:58 AM**	**958**	**6**	**15.6**	**225**	**38.9**	**6.6**	**386**	**291**	**163**	**195**	**415**	**306**	**15.1**	**228**	**30.6**	**4.8**	**293**	**265**	**154**	**156**	**339**	**296**
5/15	**7:58 AM**	**8:19 AM**	**959**	**6**	**13.5**	**221**	**40.1**	**5.8**	**387**	**286**	**150**	**194**	**262**	**297**	**14.8**	**201**	**32.8**	**5.9**	**296**	**270**	**138**	**169**	**224**	**292**
5/15	**8:19 AM**	**8:39 AM**	**960**	**6**	**15.3**	**220**	**34.9**	**5.9**	**372**	**272**	**152**	**194**	**378**	**281**	**15.0**	**170**	**30.0**	**5.0**	**278**	**253**	**143**	**155**	**324**	**279**
5/15	**8:39 AM**	**9:00 AM**	**961**	**6**	**15.0**	**220**	**39.2**	**18.0**	**361**	**279**	**149**	**192**	**325**	**284**	**13.2**	**168**	**28.3**	**7.7**	**272**	**241**	**134**	**153**	**257**	**262**
5/15	**9:00 AM**	**9:21 AM**	**962**	**6**	**13.9**	**236**	**41.3**	**5.7**	**375**	**283**	**162**	**195**	**348**	**293**	**15.1**	**189**	**29.8**	**4.8**	**299**	**260**	**142**	**166**	**281**	**283**
5/15	**9:21 AM**	**9:41 AM**	**963**	**6**	**12.5**	**209**	**33.7**	**5.9**	**388**	**278**	**150**	**194**	**305**	**292**	**12.5**	**175**	**24.3**	**4.4**	**292**	**269**	**141**	**155**	**250**	**289**
5/15	**9:41 AM**	**10:02 AM**	**964**	**6**	**4.1**	**227**	**12.6**	**2.2**	**384**	**283**	**147**	**202**	**300**	**288**	**1.9**	**172**	**10.1**	**1.7**	**285**	**265**	**141**	**149**	**239**	**283**
5/15	10:02 AM	10:22 AM	965		14.1	197	37.9	5.8	384	277	141	198	270	284	16.3	211	31.2	5.5	330	285	146	166	243	307

Table 5. XCEM Concentrations (µg/DSCM) (Cont.)

Date	START	STOP	XC RUN	M29 RUN	XCEM CONC. (µg/DSCM)										CES CONC. (µg/DSCM)									
					AS	BA	CD	CR	HG	NI	PB	SB	SN	ZN	AS	BA	CD	CR	HG	NI	PB	SB	SN	ZN
5/15	10:22 AM	10:43 AM	966	7	13.6	233	36.9	5.9	384	280	137	205	251	283	11.9	187	26.8	4.0	241	226	116	143	189	241
5/15	10:43 AM	11:03 AM	967	7	14.2	212	34.1	6.1	402	294	141	203	254	294	13.3	213	30.7	5.1	301	287	145	169	216	306
5/15	11:03 AM	11:24 AM	968	7	15.4	223	35.5	5.9	396	292	139	208	245	297	14.8	200	31.3	5.3	310	287	145	179	224	304
5/15	11:24 AM	11:45 AM	969	7	17.9	253	34.9	4.9	394	291	138	197	237	296	14.5	193	32.7	5.2	317	303	151	184	214	318
5/15	11:45 AM	12:05 PM	970	7	15.5	180	44.6	5.0	384	284	136	196	227	289	13.2	194	30.9	5.4	309	288	142	175	201	304
5/15	12:05 PM	12:26 PM	971	7	17.2	192	31.8	6.1	382	286	129	191	208	290	14.5	202	32.7	5.5	314	298	143	182	192	312
5/15	12:26 PM	12:46 PM	972	7	13.0	230	40.7	5.7	399	292	133	188	215	292	12.1	178	26.0	4.5	268	253	122	156	173	265
5/15	12:46 PM	1:07 PM	973		15.6	185	34.7	5.8	396	285	135	186	196	292	13.9	181	29.8	5.2	277	253	120	157	161	267
5/15	1:07 PM	1:27 PM	974	8	14.4	188	41.4	6.1	406	296	133	189	183	288	13.9	193	31.7	4.9	294	272	129	166	155	284
5/15	1:27 PM	1:48 PM	975	8	15.1	232	33.6	6.8	402	292	128	182	171	287	13.8	185	30.7	4.5	294	274	128	167	146	287
5/15	1:48 PM	2:09 PM	976	8	15.3	202	35.8	4.9	395	286	132	187	192	285	13.6	191	29.9	4.8	302	294	141	170	166	311
5/15	2:09 PM	2:29 PM	977	8	12.9	215	35.1	5.6	412	299	132	188	179	301	14.6	183	31.5	5.2	310	288	133	179	151	301
5/15	2:29 PM	2:50 PM	978	8	12.3	240	41.2	5.8	410	302	137	190	173	296	14.3	217	33.9	5.1	303	298	137	178	153	311
5/15	2:50 PM	3:10 PM	979	8	16.4	205	39.8	5.8	413	303	130	179	149	300	12.5	171	28.7	4.2	265	256	121	158	128	266
5/15	3:10 PM	3:31 PM	980	8	15.4	200	40.8	4.9	393	289	127	190	157	285	13.8	172	31.3	5.3	289	280	130	169	134	291
5/15	3:31 PM	3:51 PM	981		13.0	215	41.7	6.1	398	290	119	185	133	284	14.0	187	34.8	5.3	323	319	145	192	135	330
5/15	3:51 PM	4:12 PM	982	9	16.1	202	38.8	6.0	406	293	128	198	143	297	13.2	208	31.3	4.6	275	262	119	163	115	272
5/15	4:12 PM	4:32 PM	983	9	14.0	216	34.7	6.3	410	298	132	193	146	301	13.6	200	31.5	5.4	299	288	129	169	128	299
5/15	4:33 PM	4:53 PM	984	9	12.7	217	34.3	6.0	405	295	132	199	136	295	13.1	180	30.4	4.9	263	264	118	172	113	272
5/15	4:53 PM	5:14 PM	985	9	14.7	219	38.4	6.1	395	284	123	190	130	284	13.2	189	30.7	4.9	274	278	122	172	110	288
5/15	5:14 PM	5:34 PM	986	9	13.3	186	39.3	5.5	403	291	127	194	120	286	14.6	200	34.2	6.9	310	305	133	183	113	316
5/15	5:34 PM	5:55 PM	987	9	13.0	170	39.4	5.5	415	301	129	197	124	297	14.1	184	31.0	5.2	303	296	131	169	101	305
5/15	5:55 PM	6:15 PM	988		15.0	183	29.1	5.0	418	304	123	195	110	299	12.7	193	29.3	5.4	308	309	133	174	100	320
5/15	6:15 PM	6:36 PM	989		4.5	97	16.5	2.3	147	76	48	68	107	79	5.3	81	12.7	2.8	100	72	46	52	87	79
5/15	6:36 PM	6:59 PM	990		0.0	13	0.6	0.2	20	1	22	5	120	8	0.0	20	1.2	1.5	19	2	23	2	104	9
5/15	6:59 PM	7:19 PM	991		0.0	29	4.9	0.6	13	2	25	2	135	9	0.0	29	0.0	0.1	15	1	26	5	115	10
5/15	7:19 PM	7:38 PM	992		0.4	6	1.3	0.0	10	0	21	4	114	7										
5/15	7:38 PM	7:58 PM	993		0.0	29	0.1	0.4	9	0	9	0	38	3										
5/16	7:05 AM	7:25 AM	995		11.9	183	37.8	8.6	286	247	140	155	269	259	14.3	159	30.3	10.0	203	254	140	153	232	276
5/16	7:25 AM	7:45 AM	996		13.2	216	39.3	7.1	374	268	151	172	290	280	13.0	216	33.8	12.5	287	269	151	158	249	289
5/16	7:45 AM	8:06 AM	997	10	13.7	188	38.5	6.1	404	284	154	182	262	298	14.2	197	32.9	6.9	283	272	146	167	231	294
5/16	8:06 AM	8:26 AM	998	10	16.7	208	38.2	6.1	397	284	150	182	244	301	13.7	186	28.8	4.7	269	273	143	160	203	292
5/16	8:26 AM	8:47 AM	999	10	12.0	210	25.4	3.7	403	290	144	198	262	296	9.5	195	21.5	6.1	286	282	142	160	214	296
5/16	8:47 AM	9:08 AM	1	10	14.1	191	35.7	5.3	396	284	137	197	236	294	14.4	178	28.8	5.0	287	285	140	166	208	304
5/16	9:08 AM	9:28 AM	2	10	13.9	208	37.3	6.0	385	281	134	195	216	286	14.2	179	28.0	5.1	290	290	140	162	192	305
5/16	9:28 AM	9:49 AM	3	10	15.1	183	33.2	5.6	387	285	127	202	211	286	14.1	187	28.3	5.0	277	280	132	160	185	295
5/16	9:49 AM	10:09 AM	4	10	16.3	203	37.1	5.4	391	291	128	188	182	292	14.7	203	30.9	5.1	280	290	134	172	164	303
5/16	10:09 AM	10:30 AM	5		18.9	185	36.1	5.8	407	294	127	196	175	297	13.8	205	29.8	4.3	270	274	125	178	151	283

Table 5. XCEM Concentrations (µg/DSCM) (Cont.)

Date	START	STOP	XC RUN	M29 RUN	XCEM CONC. (µg/DSCM)										CES CONC. (µg/DSCM)									
					AS	BA	CD	CR	HG	NI	PB	SB	SN	ZN	AS	BA	CD	CR	HG	NI	PB	SB	SN	ZN
5/16	**10:30 AM**	**10:50 AM**	**6**	**11**	**16.2**	**183**	**34.6**	**5.3**	**393**	**286**	**126**	**202**	**163**	**281**	**14.7**	**218**	**32.0**	**4.8**	**284**	**281**	**129**	**174**	**144**	**292**
5/16	**10:50 AM**	**11:11 AM**	**7**	**11**	**15.9**	**204**	**34.1**	**5.2**	**394**	**286**	**119**	**193**	**152**	**285**	**14.7**	**209**	**32.1**	**5.4**	**302**	**305**	**136**	**185**	**141**	**315**
5/16	**11:11 AM**	**11:31 AM**	**8**	**11**	**14.4**	**193**	**35.9**	**5.8**	**382**	**280**	**118**	**183**	**143**	**278**	**15.3**	**196**	**28.8**	**7.0**	**275**	**279**	**122**	**172**	**125**	**286**
5/16	**11:31 AM**	**11:52 AM**	**9**	**11**	**10.6**	**204**	**34.3**	**4.9**	**405**	**298**	**130**	**192**	**133**	**295**	**14.5**	**206**	**29.4**	**5.2**	**288**	**298**	**128**	**182**	**119**	**309**
5/16	**11:52 AM**	**12:13 PM**	**10**	**11**	**23.1**	**194**	**37.5**	**5.4**	**405**	**289**	**112**	**191**	**128**	**290**	**14.7**	**216**	**33.5**	**5.3**	**292**	**299**	**131**	**186**	**116**	**311**
5/16	**12:13 PM**	**12:33 PM**	**11**	**11**	**12.7**	**202**	**33.5**	**5.6**	**401**	**290**	**125**	**198**	**129**	**286**	**14.4**	**226**	**30.2**	**5.0**	**274**	**291**	**128**	**179**	**111**	**301**
5/16	**12:33 PM**	**12:54 PM**	**12**	**11**	**15.6**	**201**	**30.3**	**4.9**	**374**	**273**	**115**	**189**	**110**	**269**	**12.9**	**206**	**29.2**	**7.6**	**263**	**280**	**121**	**183**	**96**	**288**
5/16	12:54 PM	1:14 PM	13		12.5	208	32.3	5.7	386	281	119	198	95	283	14.9	198	33.1	5.0	291	302	130	181	92	312
5/16	1:14 PM	1:35 PM	14		14.8	183	33.2	5.1	402	298	124	211	100	299	13.6	203	33.6	5.2	260	291	126	180	86	300
5/16	**1:35 PM**	**1:56 PM**	**15**	**12**	**15.3**	**234**	**35.4**	**5.2**	**395**	**288**	**118**	**194**	**106**	**291**	**13.9**	**203**	**31.0**	**5.1**	**286**	**301**	**130**	**191**	**97**	**308**
5/16	**1:56 PM**	**2:16 PM**	**16**	**12**	**14.3**	**234**	**33.4**	**4.9**	**389**	**289**	**118**	**196**	**105**	**279**	**14.0**	**208**	**31.8**	**6.0**	**252**	**286**	**123**	**181**	**87**	**295**
5/16	**2:16 PM**	**2:37 PM**	**17**	**12**	**12.9**	**184**	**33.9**	**5.1**	**381**	**281**	**117**	**189**	**90**	**272**	**14.7**	**191**	**30.2**	**4.9**	**264**	**291**	**124**	**178**	**80**	**301**
5/16	**2:37 PM**	**2:57 PM**	**18**	**12**	**14.6**	**179**	**35.9**	**5.2**	**376**	**284**	**113**	**195**	**82**	**273**	**14.4**	**211**	**32.5**	**5.4**	**268**	**296**	**127**	**181**	**89**	**304**
5/16	**2:57 PM**	**3:18 PM**	**19**	**12**	**16.9**	**196**	**38.8**	**5.9**	**406**	**291**	**120**	**191**	**94**	**286**	**14.5**	**213**	**32.3**	**12.4**	**274**	**297**	**127**	**189**	**85**	**303**
UNWEIGHTED AVERAGE				1	10.1	232	34.7	3.6	365	269	66	184	371	287										
				2	9.3	244	35.7	4.1	380	282	66	199	328	296										
				3	13.7	228	37.3	5.8	364	262	81	189	436	287	13.4	194	31.7	4.8	262	262	84	156	394	301
				4	14.3	210	37.6	5.8	368	269	36	189	197	276	14.5	201	32.5	5.1	301	285	39	176	184	303
				5	15.1	228	37.4	6.0	381	276	26	197	162	278	14.3	197	30.5	5.1	313	271	27	175	141	287
				6	12.9	223	34.4	5.4	379	282	153	195	333	291	12.5	186	26.6	4.9	288	260	142	158	273	283
				7	15.3	218	36.9	5.7	392	288	136	198	234	292	13.5	195	30.2	5.0	294	277	138	170	201	293
				8	14.5	212	38.3	5.7	404	295	131	186	172	292	13.8	188	31.1	4.9	294	280	131	170	148	293
				9	13.9	202	37.5	5.9	406	294	128	195	133	293	13.7	194	31.5	5.3	287	282	125	171	113	292
				10	14.6	199	35.1	5.5	395	286	139	192	230	293	13.5	189	28.5	5.4	282	282	140	164	199	298
				11	15.5	197	34.3	5.3	393	286	120	193	137	284	14.5	211	30.7	5.8	283	290	128	180	122	300
				12	14.8	205	35.5	5.3	389	286	117	193	96	280	14.3	205	31.6	6.8	269	294	126	184	87	303
				ALL	**13.7**	**216**	**36.2**	**5.3**	**385**	**281**	**100**	**193**	**236**	**287**	**13.8**	**196**	**30.5**	**5.3**	**287**	**278**	**108**	**170**	**186**	**295**
St. Dev.					**5.1**	**69**	**10.7**	**2.2**	**129**	**94**	**44**	**68**	**116**	**89**	**3.0**	**36**	**5.7**	**1.7**	**52**	**49**	**43**	**34**	**93**	**51**

The XCEM data was then averaged for each M29 run using equation 1:

$$C_i = \frac{\sum_{j=1}^{n} C_{ij} t_j}{\sum t_j}$$

Equation 1

where:

C_i	=	XCEM time-weighted concentration for element *i* during M29 test run
C_{ij}	=	XCEM reported concentration for element i during time interval j
n	=	Number of XCEM measurements during test run
t_j	=	Number of minutes XCEM measured element *i*'s concentration during time interval j coinciding with M29 sampling.
$\sum t_j$	=	M29 sampling period.

All XCEM data used for comparisons to M29 were the same as reported during M29 testing with the following four exceptions:

1. During M29 run 1, an evaluation of the calibration factors was undertaken. During this time, it was observed that Sb, Ba, and Hg calibration factors were too high relative to the calibration standards by 15%, 15%, and 7% respectively. The calibration factors were changed prior to run 2 (Appendix C).

2. Hg calibration factors were determined to be high relative to the calibration curve by 4% and were changed following the M29 test (see Appendix C for a complete discussion of Hg calibration).

3. During run 961, an unusually high Cr number (18 µg/DSCM – more than 6 SD from the average during normal spiking conditions) was observed. The spectra showed Fe, Cr, and Ni in the same ratio as stainless steel and a speck was noted on the filter tape, which was believed to be from contamination that was not representative of the stack gas. For this reason, run 961 for Cr was not used during the averaging to compare to M29.

4. The XCEM shed's air conditioning failed on May 16. As such, the Pd QA concentration did not meet the 90-110% criteria for XCEM runs 1021 and 1022, which represented 23 minutes of M29 run 12. Consequently, XCEM concentrations for run 12 were based on a time-weighted average of the 97 minutes that the XCEM produced validated data.

The modified XCEM data was submitted prior to receiving M29 results. No modification to the XCEM data was made after receiving M29 results.

2.4 XCEM CALIBRATION EVALUATION USING A QUANX – XRF AND ICP

Since XRF analysis is nondestructive, the concentrated particulate matter on the filter can be reanalyzed at a later date. In order to evaluate the XCEM calibration, CES reanalyzed

each spot using a QuanX XRF analyzer located at CES. The CES QuanX analyzer is one of four in the nation that has been approved for measuring $PM_{2.5}$ metals concentrations for EPA's speciation program. Consequently, the analyzer has undergone a series of round robin tests with other labs as well as rigorous quality control checks. The QuanX analysis was conducted approximately six weeks after M29 testing. With the exception of Hg, which appeared to be lost from the XCEM filter, the material collected on the filter seemed to be intact and representative of the sample collected at TEAD. The QuanX calibration evaluation data is shown in Table 5.

Following the reanalysis, filter spots that correlated with M29 runs 5 and 6 were combined and submitted to Columbia Analytical of Vancouver, WA for analysis using ICP/MS (Table 6).

Table 6. Analysis of XCEM Filter Tape By Columbia Analytical (µg/DSCM)

Run	As	Cd	Cr	Ba	Hg	Ni	Pb	Sb	Sn	Zn
5	14.0	36.4	5.0	176	274	226	22	174	74	252
6	13.3	34.2	4.7	159	254	220	129	152	127	245

2.5 PRECISION

Five elements were spiked by MSE-TA at a constant rate throughout the testing: Ba, Hg, Ni, Sb, and Zn. Although Ba and Zn had background concentrations of about 10%, their limited variability during testing affected the predicted concentrations precision by only a few percent. Overall, these elements were spiked with a precision of better than five percent (Table 7).

Both the XCEM and M29 show good precision for these elements with the XCEM precision about 30% lower than M29.

Table 7. Predicted, XCEM and Method 29 Precision During Validation Testing[1]

APPROACH	HG	SB	NI	BA	ZN
PREDICTED	1.0	1.7	1.1	5.9	3.5
XCEM	3.8	2.5	3.7	6.9	2.4
M29	6.1	6.1	5.7	7.2	3.3

1) Determined by percent RSD of 12 concentrations reported for M29 runs.

3.0 DISCUSSION

3.1 REGULATED ELEMENTS TYPICALLY FOUND IN THE FEEDSTREAM

Although APE-1236 is regulated for nine elements, only three elements, Pb, Cd, and Cr, are found in high enough quantities in stack emissions to potentially limit incineration feed rates (Table 8). The XCEM successfully measured all three of the key elements and

met the 20% relative accuracy requirements in proposed PS-10 with relative accuracies of 4%, 17%, and 15% respectively.

Table 8. TEAD Emission Limits

Elem	State Limit		MACT Limit	Potential to Limit Feed Rate
	g/hr	µg/dscm[1]	µg/DSCM	
Pb	4.3	932	240	Yes
Cd	0.26	56		Yes
Cr	0.04	10	97	Yes
As	0.11	24		No
Hg	14	3,036	130	No
Sb	14	3,036	NR	No
Ni	930	201,740	NR	No
Ba	2,400	521,243	NR	No
Zn	NR	NR	NR	No

1) Assumes 4635 DSCM per hour
NR: Not regulated

3.1.1 LEAD

Lead is the element which most often limits incineration rates at APE-1236. The TEAD incinerator has a state-mandated Pb stack emission limitation of 4.3 g/hr. At typical stack flow rates, this equates to about 900 µg/DSCM. EPA's Hazardous Waste Combustor Maximum Achievable Control Technology (MACT) rules, which are scheduled for implementation within two years, will further limit the combined Pb and Cd emission rate to 240 µg/DSCM.

Currently, Pb concentrations within the munitions are determined for each type of ordnance prior to incineration. Munition feed rates into the incinerator are restricted using a model which assumes that a fraction of the lead in the munitions will be transported through the air pollution control devices and emitted from the stack. The effectiveness of the model is dependent upon several assumptions including transport under various meteorological regimes, incinerator temperature effects, and chemical interactions. Direct measurement of Pb concentrations in the stack gas allows for improved understanding of the relationship between munitions incineration and stack emission rates as well as an enhanced mechanism for regulating feed rates.

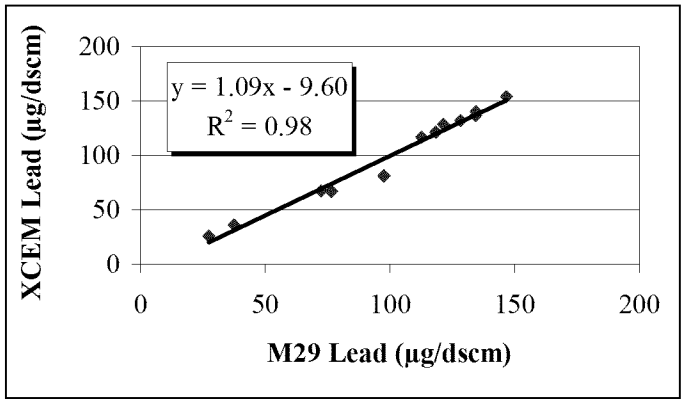
Table 9 shows the Pb results for the MSE/background predicted concentrations (PRD), M29, XCEM, the post-test analysis of the XCEM spots using the CES QuanX (QN), and the ICP/MS analysis of the XCEM filter tape by Columbia Analytical (CA). In general, the results are in very good agreement with the PRD, M29, XCEM, and QN concentrations agreeing to within seven percent. The XCEM and M29 Pb concentrations are also highly correlated with an r^2 of 0.98 (Figure 3).

Lead in the first five M29 runs was exclusively from residual concentrations in the TEAD incinerator. Following run five, MSE-TA began spiking an additional 105 µg/DSCM of Pb. During testing both M29 and the XCEM reported concentrations ranging from 25 to 150 µg/DSCM. The relative accuracy for the XCEM was 4.4%. This good agreement between the XCEM and M29 demonstrates the capability of the XCEM to accurately measure Pb at the incinerator under a wide range of concentrations.

Table 9. Summary of Lead Concentration Data During M29 Testing (µg/DSCM)

RUN	PRD	M29	XC	QN	CA	XC/QN	XC/PRD	M29/PRD	XC/M29	QN/M29
1	67	72	67	68		0.99	1.01	1.08	0.93	0.94
2	61	77	67	64		1.04	1.11	1.27	0.87	0.84
3	77	98	81	84		0.97	1.06	1.27	0.83	0.86
4	41	38	36	39		0.93	0.88	0.93	0.95	1.03
5	36	27	26	26	22	0.99	0.73	0.77	0.94	0.95
6	167	147	154	141	129	1.09	0.92	0.88	1.05	0.96
7	150	135	137	141		0.97	0.91	0.90	1.01	1.05
8	140	128	132	132		1.00	0.94	0.92	1.03	1.03
9	134	122	128	125		1.02	0.95	0.91	1.05	1.03
10	151	135	140	140		1.00	0.93	0.89	1.04	1.04
11	136	118	121	129		0.94	0.89	0.87	1.02	1.09
12	128	113	117	126		0.93	0.91	0.88	1.04	1.12
AVG.	**107**	**101**	**101**	**101**	**75**	**0.99**	**0.94**	**0.96**	**0.98**	**0.99**
SD	**47**	**39**	**43**	**43**	**76**	**0.05**	**0.09**	**0.16**	**0.07**	**0.09**

Figure 3. XCEM vs. M29 Lead for Validation Tests



3.1.2 CADMIUM

The APE-1236 state-mandated emission limit for Cd is about 60 µg/DSCM under typical stack flow rates. Cadmium stack concentrations, which are derived from incineration of shell casings, can occasionally approach this limit. For this test, approximately 80% of the stack's Cd was from MSE-TA while 20% was estimated to be background. Table 10 shows the M29 and XCEM results for Cd during the validation tests.

Overall, the XCEM and M29 were in good agreement for Cd. On average, the XCEM was about 14% higher than M29 with a relative accuracy of 17%. The reanalysis of the

XCEM filter tape yielded mixed results with the QuanX XRF within 3% of M29 and the Columbia Analytical concentrations within 4% of the XCEM. The inconsistency between the XCEM and CES-QuanX results suggests that an XCEM calibration error may have been responsible for the difference between M29 and the XCEM.

Table 10. Summary of Cadmium Concentration Data During M29 Testing (µg/DSCM)

RUN	PRD	M29	XC	QN	CA	XC/QN	XC/PRD	M29/PRD	XC/M29	QN/M29
1	41.5	29.4	35.2	29.3		1.20	0.85	0.71	1.20	0.99
2	39.8	32.0	35.8	29.4		1.22	0.90	0.80	1.12	0.92
3	48.6	34.6	37.2	31.6		1.18	0.77	0.71	1.08	0.91
4	41.6	31.0	37.7	32.6		1.16	0.91	0.74	1.22	1.05
5	41.4	30.8	36.4	30.0	36.4	1.22	0.88	0.74	1.18	0.97
6	45.4	31.2	37.2	28.6	34.2	1.30	0.82	0.69	1.19	0.92
7	43.7	31.8	36.6	30.9		1.19	0.84	0.73	1.15	0.97
8	41.5	32.4	37.7	31.1		1.21	0.91	0.78	1.16	0.96
9	40.5	32.0	37.4	31.5		1.19	0.92	0.79	1.17	0.98
10	41.1	29.8	34.6	27.9		1.24	0.84	0.73	1.16	0.94
11	39.9	31.3	34.9	30.9		1.13	0.87	0.78	1.12	0.99
12	39.0	31.2	35.5	31.6		1.12	0.91	0.80	1.14	1.01
AVG.	**42.0**	**31.5**	**36.4**	**30.4**	**35.3**	**1.20**	**0.87**	**0.75**	**1.16**	**0.97**
SD	**2.7**	**1.3**	**1.1**	**1.4**	**1.5**	**0.05**	**0.05**	**0.04**	**0.04**	**0.04**

3.1.3 CHROMIUM

APE-1236 has an effective Cr emission limit of less than 10 µg/DSCM under typical stack operating conditions. Since the background Cr concentrations were uncertain at the start of the validation test, MSE-TA spiked a nominal 3 µg/DSCM during M29 runs 1 and 2. Following these runs, it was determined that the background Cr concentrations were insignificant and MSE-TA raised their spiking rate to 5 µg/DSCM for the remainder of the tests. Overall, the XCEM was consistently 10% higher than M29 at both concentration levels (Table 11). This represents a difference of about 0.5 µg/DSCM. The good agreement between the XCEM and M29 at both the 3 and 5 µg/DSCM levels validates the ability of the XCEM to accurately measure Cr at very low concentrations.

Subsequent measurements of the XCEM filter tape by the CES-QuanX and ICP were within 3% of the M29 concentrations. The consistency of M29 with the predicted values and subsequent measurements of the XCEM filter tape indicates that an XCEM calibration error of about 10% may have been responsible for any differences between the two methods.

The Cr relative accuracy was 15%, meeting PS10 criteria.

Table 11. Summary of Chromium Concentration Data During M29 Testing (µg/DSCM)

RUN	PRD	M29	XC	QN	CA	XC/QN	XC/PRD	M29/PRD	XC/M29	QN/M29
1	2.9	3.6	3.7	3.2		1.16	1.28	1.24	1.03	0.89
2	2.9	4.0	4.0	3.2		1.27	1.39	1.38	1.01	0.79
3	5.2	6.4	5.8	4.8		1.20	1.11	1.24	0.90	0.75
4	5.0	5.0	5.8	5.1		1.14	1.15	0.99	1.16	1.02
5	5.0	5.2	6.1	5.0	5.0	1.22	1.21	1.04	1.16	0.96
6	5.0	4.8	5.8	5.3	4.7	1.09	1.16	0.97	1.20	1.10
7	5.1	4.9	5.6	5.2		1.09	1.10	0.96	1.15	1.05
8	5.1	5.1	5.8	4.8		1.20	1.13	1.00	1.14	0.95
9	5.1	5.2	5.9	5.3		1.10	1.17	1.02	1.14	1.03
10	4.8	4.9	5.4	5.4		1.01	1.14	1.03	1.11	1.10
11	5.0	4.8	5.4	5.5		0.97	1.07	0.96	1.11	1.15
12	5.1	4.8	5.3	6.9		0.76	1.04	0.95	1.10	1.44
AVG.	**4.7**	**4.9**	**5.4**	**5.0**	**4.8**	**1.10**	**1.16**	**1.07**	**1.10**	**1.02**
SD	**0.8**	**0.7**	**0.8**	**1.0**	**0.2**	**0.14**	**0.09**	**0.14**	**0.08**	**0.18**

Overall, the XCEM effectively measured the three key elements for the M29 tests. The XCEM met relative accuracy criteria, showed good response to changes in concentration, and had good response times and correlations.

3.2 REGULATED ELEMENTS NOT TYPICALLY FOUND IN TEAD EMISSIONS

APE-1236 is regulated for six additional elements that are not typically found in the feedstream in quantities that approach the regulatory limits: As, Hg, Sb, Ni, Ba, and Be. The XCEM did not measure Be as part of this test. The XCEM met PS10 measurement criteria for Sb (20%) and Ba (4%), but was conservatively higher than M29 for As, Hg, and Ni with relative accuracies of 27%, 33%, and 33% respectively.

3.2.1 ARSENIC

Arsenic results are shown in Table 12. The XCEM reported concentration was in good agreement with the post-test analysis of the filter tape by both the QuanX and Columbia Analytical. Their agreement indicates that the XCEM calibration was correct to within a few percent.

The XCEM concentration is also in good agreement with the predicted concentration. Some question exists, however, as to the predicted concentrations true value since the HKM analysis of the MSE-TA solution was 23% lower for As. If the HKM As concentrations were used, the predicted concentration would be much closer to M29.

Overall, the XCEM was 25% higher than M29 concentrations for As. Aside from calibration errors, other potential sources of error for the XCEM include loss during transport, low filter trapping efficiency, deposit positioning errors, spectral interferences,

and incorrect flow measurements. Each of these error sources is highly unlikely. The first three sources of error would only result in XCEM concentrations lower than M29. Spectral interferences would not have impacted Columbia Analytical ICP/MS results, and incorrect flow measurements would have resulted in all metals being uniformly high or low since one XCEM flow measurement is applied to all of the metals for each run. For this reason, the differences in concentration appear to be due to M29 errors.

The XCEM's relative accuracy of 27% did not meet PS10 criteria. However, the XCEM was conservatively high for this element, which is typically not found in the TEAD emissions. The XCEM was also highly correlated with M29 As (r^2=0.85) showing good responsiveness to changes in As concentration.

Table 12. Summary of Arsenic Concentration Data During M29 Testing (µg/DSCM)

RUN	PRD	M29	XC	QN	CA	XC/QN	XC/PRD	M29/PRD	XC/M29	QN/M29
1	10.6	7.8	10.1	9.4		1.07	0.95	0.74	1.29	1.20
2	10.7	8.3	9.3	10.2		0.91	0.88	0.77	1.13	1.24
3	16.7	11.5	13.7	13.4		1.02	0.82	0.69	1.19	1.17
4	16.1	11.9	14.3	14.5		0.98	0.89	0.74	1.20	1.22
5	16.1	11.8	15.3	14.1	14.0	1.09	0.95	0.73	1.30	1.20
6	16.0	11.3	13.9	13.8	13.3	1.01	0.87	0.71	1.23	1.22
7	16.4	11.7	15.6	13.7		1.14	0.96	0.71	1.34	1.18
8	16.2	12.3	14.4	13.8		1.05	0.89	0.76	1.18	1.12
9	16.2	12.2	13.9	13.7		1.02	0.86	0.75	1.14	1.12
10	15.2	11.1	14.3	13.3		1.07	0.94	0.73	1.28	1.20
11	16.0	11.7	15.5	14.7		1.05	0.97	0.73	1.32	1.25
12	16.2	11.9	14.8	14.3		1.03	0.91	0.73	1.24	1.21
AVG.	**15.2**	**11.1**	**13.8**	**13.3**	**13.7**	**1.04**	**0.91**	**0.73**	**1.24**	**1.19**
SD	**2.2**	**1.5**	**2.0**	**1.7**	**0.5**	**0.06**	**0.05**	**0.02**	**0.07**	**0.04**

3.2.2 MERCURY

Unlike the other elements, Hg is primarily in the vapor phase in typical stack emissions. For example, during the 2001 M29 tests at TEAD, the particulate Hg captured on the M29 filter and probe represented 1% of the total Hg. The XCEM relies upon a specially treated filter membrane to capture the vapor phase Hg while M29 uses an impinger train.

The APE-1236 Hg limit is about 3000 µg/DSCM. Mercury, however, is typically not present in TEAD stack emissions. Indeed, an earlier multi-metals monitor was certified for use at TEAD without even measuring Hg (Seltzer, 1999). For the current validation test, Hg was spiked by MSE-TA with results shown in Table 13.

The XCEM and M29 concentrations had acceptable agreement during runs 1-5 with the XCEM 16% higher than M29. Had the conditions for runs 1-5 been duplicated for nine runs, the XCEM would have met the relative accuracy requirements for Hg. However, following run 5, the XCEM was consistently 34% higher than M29. It is believed that these differences are due to vaporization of particulate mercury from the M29 filter.

During runs 1-5, the Hg solution contained Zn and Ni. Following run 5, Pb was added to this solution. Although Hg was spiked at a constant rate, M29 Hg concentrations decreased by 8% following Pb injection. The source of this decrease may be related to the unusually high level of particulate phase Hg present during this validation test. Particulate Hg is captured on the M29 quartz fiber filter and can be readily volatilized if the filter is not cooled. Even though total M29 Hg decreased following run 5, the fraction of Hg on the M29 filter increased from 18% in runs 1-5 to 30% in runs 6-12 (Pattison, 2002). The Hg captured on the filter represents particulate phase Hg, which is typically only a couple of percent of the total Hg. As such, M29 does not require refrigeration of the M29 filter and it was not cooled while being trucked to California for analysis. During this time, a significant quantity of the Hg on the filter could have vaporized. Figure 4 shows the relationship between the level of Hg on the M29 filter and the percent difference between M29 and the XCEM. The high correlation (r^2 =

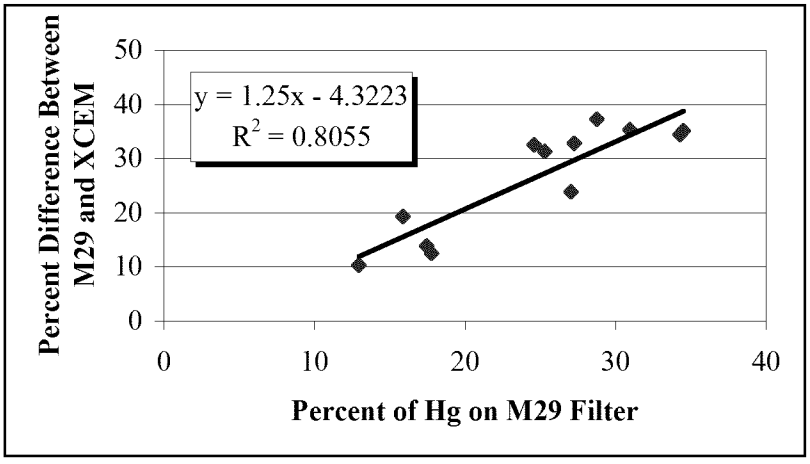
The XCEM filter also showed a loss of about 30% of its Hg as demonstrated by an analysis of the spectra available during validation testing and a few weeks later when the tape was reanalyzed by the CES QuanX. Interestingly, the CES tape had previously shown good retention for vapor phase Hg on earlier tests (Cooper, 2000; Johnsen, 2001) so the Hg loss seems to be dependent upon the quantity in the particulate phase.

Table 13. Summary of Mercury Concentration Data During M29 Testing (µg/DSCM)

RUN	PRD	M29	XC	QN[1]	CA[1]	XC/QN	XC/PRD	M29/PRD	XC/M29	QN/M29
1	324	332	367	257		1.42	1.13	1.02	1.10	0.77
2	325	334	381	251		1.52	1.17	1.03	1.14	0.75
3	333	294	365	262		1.39	1.09	0.88	1.24	0.89
4	322	327	368	301		1.22	1.14	1.02	1.13	0.92
5	323	318	379	308	274	1.23	1.18	0.99	1.19	0.97
6	329	280	378	288	254	1.31	1.15	0.85	1.35	1.03
7	327	285	392	302		1.30	1.20	0.87	1.37	1.06
8	325	306	406	294		1.38	1.25	0.94	1.33	0.96
9	324	309	405	287		1.41	1.25	0.95	1.31	0.93
10	328	292	395	282		1.40	1.20	0.89	1.35	0.97
11	326	295	397	286		1.39	1.22	0.90	1.35	0.97
12	322	293	389	267		1.46	1.21	0.91	1.33	0.91
AVG.	**326**	**305**	**385**	**282**	**264**	**1.37**	**1.18**	**0.94**	**1.27**	**0.93**
SD	**3.3**	**19**	**14**	**19**	**13.8**	**0.09**	**0.05**	**0.06**	**0.10**	**0.09**

1) Mercury lost from filter.

Figure 4. Percent Difference Between M29 and the XCEM vs. Percent of Mercury on M29 Filter



3.2.3 ANTIMONY

Antimony results are shown in Table 14. Overall, the XCEM was higher than M29 by about 18%, but met relative accuracy criteria with an RA of 19.9%. Subsequent analysis of the filter tape by the CES QuanX was in better agreement with M29. For this reason, it is believed that the XCEM/M29 differences were due to XCEM calibration errors of about 15%.

Table 14. Summary of Antimony Concentration Data During M29 Testing (µg/DSCM)

RUN	PRD	M29	XC	QN	CA	XC/QN	XC/PRD	M29/PRD	XC/M29	QN/M29
1	192	151	184	166		1.10	0.96	0.79	1.21	1.10
2	196	182	200	177		1.12	1.02	0.93	1.10	0.97
3	201	183	190	156		1.21	0.94	0.91	1.03	0.85
4	194	166	189	176		1.08	0.98	0.85	1.14	1.06
5	193	168	195	172	174	1.14	1.01	0.87	1.16	1.03
6	199	162	194	159	152	1.22	0.98	0.81	1.20	0.98
7	197	164	198	174		1.14	1.01	0.83	1.21	1.06
8	192	162	186	170		1.09	0.97	0.84	1.15	1.05
9	189	157	195	171		1.14	1.03	0.83	1.25	1.09
10	194	157	193	162		1.19	0.99	0.81	1.23	1.03
11	193	163	193	180		1.07	1.00	0.84	1.18	1.10
12	190	154	193	183		1.05	1.01	0.81	1.25	1.19
AVG.	**194**	**164**	**192**	**171**	**163**	**1.13**	**0.99**	**0.84**	**1.18**	**1.04**
SD	**3**	**10**	**5**	**8**	**15**	**0.06**	**0.03**	**0.04**	**0.06**	**0.08**

3.2.4 NICKEL

Validation test results for Ni are reported in Table 15. The XCEM was about 30% higher than M29 and had a relative accuracy of 34%, which did not meet PS10 criteria. Although the XCEM Ni concentrations were supported by the CES QuanX filter evaluation and predicted concentrations, the M29 results were similar to results from Columbia Analytical. At this time, the XCEM appears to have been calibrated correctly. As discussed in the As section, since the XCEM was higher than M29, the difference appears to be due to M29 analytical problems.

Nickel is not typically found in TEAD stack emissions and the site has a 140,000 µg/DSCM stack emission limit. As such, the conservative numbers produced by the XCEM should serve to adequately ensure that Ni is below the emission limit.

Table 15. Summary of Nickel Concentration Data During M29 Testing (µg/DSCM)

RUN	PRD	M29	XC	QN	CA	XC/QN	XC/PRD	M29/PRD	XC/M29	QN/M29
1	267	200	270	262		1.03	1.01	0.75	1.35	1.31
2	268	235	283	276		1.02	1.06	0.88	1.20	1.18
3	275	234	262	262		1.00	0.95	0.85	1.12	1.12
4	265	213	269	285		0.95	1.02	0.80	1.26	1.34
5	266	231	274	267	226	1.03	1.03	0.87	1.19	1.15
6	271	225	281	259	220	1.08	1.03	0.83	1.25	1.15
7	269	218	289	285		1.01	1.07	0.81	1.33	1.31
8	267	219	296	281		1.05	1.11	0.82	1.35	1.28
9	266	221	294	283		1.04	1.11	0.83	1.33	1.28
10	270	205	285	281		1.02	1.06	0.76	1.39	1.37
11	268	216	288	292		0.99	1.07	0.81	1.33	1.35
12	266	199	286	294		0.98	1.08	0.75	1.44	1.48
AVG.	**268**	**218**	**281**	**277**	**223**	**1.02**	**1.05**	**0.81**	**1.30**	**1.28**
SD	**2.8**	**12**	**10**	**12**	**4.9**	**0.04**	**0.04**	**0.04**	**0.09**	**0.11**

3.2.5 BARIUM

Barium results for the validation tests are shown in Table 16. For Ba, the predicted concentrations, M29 results, XCEM results, and QuanX reanalysis all agree to within 10% with an XCEM relative accuracy of 4%. Although the stack limit is 500,000 µg/DSCM, typical Ba concentrations found in the stack are in the 0 to 200 µg/DSCM range. During these validation tests, the XCEM demonstrated good accuracy relative to M29 for Barium under realistic stack conditions.

Table 16. Summary of Barium Concentration Data During M29 Testing (µg/DSCM)

RUN	PRD	M29	XC	QN	CA	XC/QN	XC/PRD	M29/PRD	XC/M29	QN/M29
1	237	214	229	204		1.12	0.96	0.90	1.07	0.95
2	238	248	244	222		1.10	1.03	1.05	0.98	0.89
3	253	247	228	195		1.17	0.90	0.98	0.92	0.79
4	223	203	210	201		1.04	0.94	0.91	1.03	0.99
5	218	207	230	194	176	1.18	1.05	0.95	1.11	0.94
6	240	216	222	186	159	1.19	0.92	0.90	1.03	0.86
7	229	212	215	197		1.09	0.94	0.92	1.02	0.93
8	218	210	215	189		1.14	0.99	0.97	1.02	0.90
9	212	206	202	193		1.04	0.95	0.98	0.98	0.94
10	226	208	198	187		1.06	0.88	0.92	0.95	0.90
11	215	210	197	211		0.93	0.92	0.98	0.94	1.00
12	209	204	203	206		0.98	0.97	0.98	0.99	1.01
AVG.	**226**	**216**	**216**	**199**	**167**	**1.09**	**0.96**	**0.95**	**1.00**	**0.93**
SD	**13**	**16**	**15**	**11**	**13**	**0.08**	**0.05**	**0.04**	**0.05**	**0.06**

3.3 NONREGULATED METALS

Two non-regulated metals, Sn and Zn, were measured by the XCEM during validation testing. As discussed earlier, M29 is not approved for Sn and the M29 Sn results were not considered valid (Pattison, 2002b). Zinc was spiked by MSE-TA with XCEM reported concentrations shown in Table 17.

Overall, the XCEM Zn concentrations were consistently about 40% higher than M29. The XCEM Zn concentrations were in good agreement with both the CES QuanX and Columbia Analytical tape evaluations indicating that calibration was not the primary source of this difference. As discussed in the arsenic section, XCEM potential sources of error would lead to decreased concentrations. Since the XCEM was higher than M29, it is believed that the difference is primarily due to M29 errors.

Table 17. Summary of Zinc Concentration Data During M29 Testing (µg/DSCM)

RUN	PRD	M29	XC	QN	CA	XC/QN	XC/PRD	M29/PRD	XC/M29	QN/M29
1	300	195	288	294		0.98	0.96	0.65	1.48	1.51
2	297	212	297	303		0.98	1.00	0.71	1.40	1.43
3	312	215	287	301		0.96	0.92	0.69	1.34	1.40
4	285	196	276	303		0.91	0.97	0.69	1.40	1.54
5	283	196	277	282	252	0.98	0.98	0.69	1.41	1.44
6	301	209	291	283	245	1.03	0.97	0.69	1.39	1.35
7	291	202	292	301		0.97	1.00	0.69	1.45	1.49
8	285	204	293	294		1.00	1.03	0.72	1.44	1.44
9	280	202	293	293		1.00	1.05	0.72	1.45	1.45
10	292	199	293	298		0.98	1.00	0.68	1.47	1.50
11	283	203	286	303		0.94	1.01	0.72	1.41	1.49
12	278	196	279	302		0.92	1.01	0.71	1.43	1.54
AVG.	**290**	**202**	**288**	**296**	**248**	**0.97**	**0.99**	**0.70**	**1.42**	**1.47**
SD	**10**	**7**	**7**	**7**	**5**	**0.03**	**0.03**	**0.02**	**0.04**	**0.06**

4.0 CONTINUED USE OF THE XCEM

Following the conclusion of the M29 tests, the XCEM was used in a series of diagnostic tests to evaluate air pollution control technology installed at APE-1236. Using the XCEM, TEAD personnel developed baseline data for lead and zinc during incineration of various munitions. Next, a bypass duct was blocked with a metal plate resulting in a greater than 90% drop in metal concentrations. Using this data, TEAD was better able to understand sources of Pb in the emissions.

Currently, the XCEM is being moved to a newly developed “test furnace” at TEAD. The furnace, operated by the Ammunition Equipment Division, anticipates using the instrument to rapidly determine effects of changes in munitions or control strategies.

The continued use of the XCEM to diagnose and assist with process control indicates the value of having an installed continuous emission monitor for multi-metals at TEAD.

5.0 CONCLUSION AND RECOMMENDATIONS

The XCEM successfully measured the three potential emission limiting elements found in APE-1236 which could potentially approach emission limits: Pb, Cd, and Cr. The XCEM also successfully measured two other regulated metals: Ba and Sb and were conservatively high for As, Hg, Ni and the unregulated Zn. An analysis of potential sources of error suggests that the XCEM numbers for As, Hg, Ni, and Zn best reflect actual stack gas concentrations. The XCEM was responsive to changes in concentration and showed good correlation with the reference method for elements that were spiked at more than one level. In addition, the XCEM successfully measured low metal concentrations as demonstrated by the XCEM's tracking of M29 chromium's low concentrations when changes of only two micrograms per cubic meter occurred between runs two and three.

The XCEM has continued to be a useful instrument at TEAD for diagnostics and process control. CES recommends the adoption of the XCEM as a validated monitor for incinerators such as APE-1236. Recent advances in XRF technology have allowed for a miniaturized version of the XCEM with better detection limits than the current system. CES also recommends that this technology be incorporated into a mobile version of the XCEM for the army's stack testing organization (CHPPM) and an extension of the technology to a mercury-dedicated XCEM.

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APPENDIX B

MERCURY CALIBRATION ADJUSTMENTS AND VOLATILITY LOSSES FROM PARTICULATE MATTER FRACTION

1. INTRODUCTION

Mercury represents a distinctly different hazardous element from the others included in this test in that it is more likely to exist in the vapor phase and has been shown to exhibit distinctly different transport properties. These properties appear to have contributed to differences in the mercury concentrations measured by the different methods compared in this test. This appendix discusses the details associated with both the adjustments that were made to the XCEM calibration factors and losses of mercury from particulate deposits after sample collection.

2. CALIBRATION ADJUSTMENTS

Two adjustments were made to the mercury results after the first test run was started. The first adjustment was a 7% increase in the mercury sensitivity factor between M29 Run 1 and Run 2. The second was a 4% increase in the sensitivity factor shortly after the completion of the tests and before the M29 and XCEM results were submitted. The necessity for these adjustments was due in part to the volatility of the mercury, which makes it difficult to make stable thin-film mercury standards. As such, thin film mercury standards are not available from NIST. The standards that are available are relatively unstable and need to be frequently validated. This method limitation is generally minimized by the fact that energy dispersive X-ray fluorescence sensitivity factors are a smoothly varying function of atomic number. This allows mercury sensitivity factors to be estimated by interpolation using well-defined sensitivity factors for elements with similar atomic number such as platinum, gold, thallium, lead and bismuth. The following two adjustments were based on this interpolation process and a re-evaluation of the best-estimated calibration factor.

a. Adjustments During First Day of Testing

Mercury calibration of the XCEM prior to the M29 tests was done during preliminary spiking tests. During these tests, the NIST thin film standard for lead was not available and the mercury sensitivity was estimated based on a previous measurement of the lead NIST standard. This fact wasn't realized until the testing started and a review of the preliminary mercury results indicated a potential bias relative to the NIST lead results. As a result, the mercury calibration was adjusted by 7% during the period between M29 Run 1 and Run 2.

b. Post-Test Adjustments

The second adjustment to the mercury results of 4% was applied when the calibration factors were reviewed following the tests. A comparison with the ratio of mercury to lead sensitivity factors developed from a more extensive study in the laboratory indicated that the 0.838 ratio used during the tests should have been 0.873. This 4% correction was applied to the XCEM results prior to the submission of either the M29 or the XCEM results.

3. LOSSES FROM PM FRACTION

a. Introduction

The XCEM mercury results were, on average, 18% greater than the predicted concentration, 27% greater than the M29 results, 37% greater than the laboratory XRF measurements of the XCEM deposit spots, and 45% greater than the CVAA measurements on the XCEM deposit spots. Subsequent investigations of these differences strongly suggest that the XCEM results are the best estimate of the actual mercury concentrations in the stack. It is hypothesized that the large differences between the XCEM mercury results and the results from the other methods is due to the loss of mercury from the filter deposits after the M29 and XCEM samples were collected and after the XCEM original measurements were made. This hypothesis is described in more detail in the following subsection. The experimental measurements are described in Subsection C and the results are summarized and discussed in Subsection D. The hypothesized model is then evaluated relative to the available data in Subsection E.

b. Model

A model has been developed to explain the apparent high XCEM mercury concentrations relative to M29. In this model, mercury is lost from the particulate fraction of the M29 and XCEM filters after the initial XCEM measurements were made. That is, a substantial fraction of mercury was associated with the particulate fraction, and the mercury in this particulate was unstable. Since all of the other analytical methods relied on aged samples, the mercury concentration results were low due to vaporization of particulate mercury prior to laboratory analysis. As discussed in the following subsection, a substantial amount of experimental data is available, all of which is supportive of this hypothesized model. Most of this experimental data was developed only because of the unique characteristics of the XCEM and the fact that the XCEM elemental measurement is nondestructive and the spectra from each of the original measurements were archived.

c. Experimental

The initial XCEM measurements were based on the analysis of filter deposits, which were a combination of both absorbed vapor phase mercury species and surface deposits of particulate mercury species. Each deposit was analyzed using three different X-ray excitation conditions, resulting in spectra that were used to determine concentration. All spectra were archived in the XCEM computer. As such, the deposit was available for further analysis and testing, and the original spectra was available for comparison with subsequently developed spectra.

Following the validation testing at TEAD, several tests were conducted by CES to better understand the mercury concentration differences between M29 and the XCEM.

- All of the XCEM deposit spots corresponding to all of the M29 runs were reanalyzed by CES's laboratory QuanX XRF analyzer six weeks after the initial validation test. In addition, ten XCEM filter deposit spots were analyzed over a period of two months to evaluate mercury stability. Spectra from these tests were compared to archived spectra from the original validation test.

- The XCEM deposit spots corresponding to M29 Runs 5 and 6 were analyzed first by laboratory XRF and then by cold vapor atomic absorption by an independent laboratory (Columbia Analytical Services).

- The elemental concentrations in the MSE-TA spiking solutions corresponding to M29 Runs 5 and 6 were analytically determined by HKM labs in Butte, MT.

d. Results and Discussion

The mercury results for the original validation test are summarized in Table C1. There is a clear bias of about 26% between the XCEM results and the M29 results. Normally, the M29 results would be accepted as the best estimate of stack mercury concentration and it would be assumed that the candidate method (XCEM) was in error. However, because of the total quality assurance associated with the XCEM and the fact that the XRF analysis is non-destructive, it is possible to conduct further analyses to evaluate the potential cause of this difference. Additionally, the laboratory analysis results for each component of the M29 sampling trains (i.e. probe, filter, and back half) were determined separately, and are available for interpretation.

Table C.1 Mercury Reported Concentrations During Year 2002 Method 29 Validation Testing.

RUN	PRD	M29	XC	QN	CA	PRD	XC	QN	CA
	µg/DSCM					Normalized to M29			
1	324	332	367	257		0.98	1.10	0.77	
2	325	334	381	251		0.97	1.14	0.75	
3	333	294	365	262		1.13	1.24	0.89	
4	322	327	368	301		0.98	1.13	0.92	
5	323	318	379	308	274	1.02	1.19	0.97	0.86
6	329	280	378	288	254	1.18	1.35	1.03	0.91
7	327	285	392	302		1.15	1.37	1.06	
8	325	306	406	294		1.06	1.33	0.96	
9	324	309	405	287		1.05	1.31	0.93	
10	328	292	395	282		1.13	1.35	0.97	
11	326	295	397	286		1.11	1.35	0.97	
12	322	293	389	267		1.10	1.33	0.91	
AVG.	**326**	**305**	**385**	**282**	**264**	**1.07**	**1.27**	**0.93**	**0.88**
SD	**3.3**	**19**	**14**	**19**	**13.8**	**0.07**	**0.10**	**0.09**	**0.03**

i. Loss of Mercury From the XCEM Filter

a. Laboratory XRF Measurements (QN)

Two months after the validation testing, CES's laboratory QuanX XRF analyzer reanalyzed the original XCEM deposit samples with good replication for all elements except mercury (see Table 5 in main body of text).

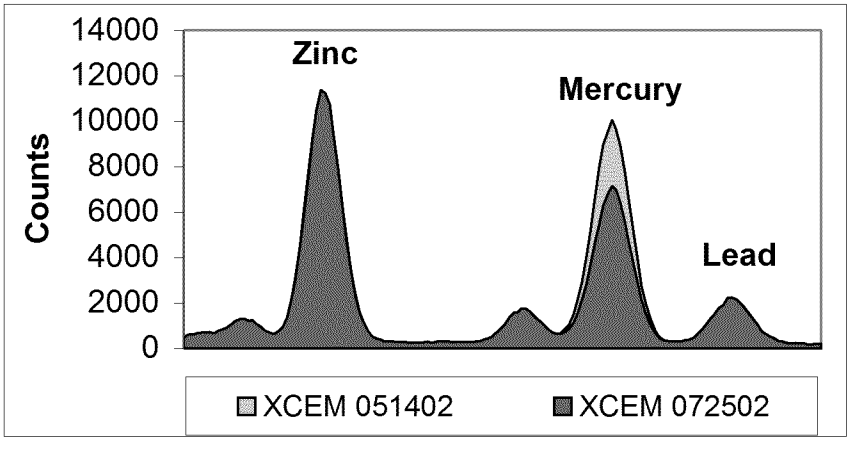
A series of ten spots on the XCEM filter tape were reanalyzed between on 6/21/02 and 7/11/02. The spots, which represent 10 XCEM runs, showed a consistent mercury loss of about 30% over the three-week period. Other sources of error such as shifts in geometry or instrument instability were eliminated as possible systematic sources of error by noting that the other elements were replicated within experimental error to a few percent.

b. XCEM Measurements (XCEM)

To confirm this loss of mercury, five XCEM deposit spots were re-analyzed by the TEAD XCEM, which was still operating with the same conditions and calibration factors as used during the M29 tests about two months earlier. The X-ray spectra from the original analysis of XCEM Run Numbers 939 to 943 (M29 Run Number 4) are compared in Figure C1. This comparison clearly shows that there is good agreement for the two closest analyte peaks for zinc and lead, but a substantial reduction in the peak intensity for the mercury L-alpha analyte line. A comparison of the XCEM mercury concentrations measured during the M29 testing (5-14-02) with those measured with the XCEM on 7-25-02 indicate a 31.4 ± 0.4 μg/m3 reduction in measured concentration. Although this reduction might be associated with possible systematic errors such as sample positioning, this possible source of error was eliminated by comparing other elements such as zinc and lead as well as the ratio of mercury to these elements. The reduction in mercury to zinc ratio, for example, was 29.1%, which is in good agreement with the mercury-measured reduction.

Clearly, mercury was lost from the XCEM deposit after the sample was collected and analyzed by the XCEM. As discussed in the following subsection, the available data strongly suggests that a substantial portion of the M29 mercury was also lost from the M29 PM filter deposits prior to analysis.

Figure C.1 Comparison of XCEM X-Ray Spectra Measured During Method 29 Testing and Seventy-One Days Later.



ii. Instability of M29 Mercury PM Deposit Highly Likely

Although there is no direct evidence of the loss of mercury from the M29 samples, there is ample indirect evidence that a similar loss to that of the XCEM deposit would be expected. This indirect evidence is discussed in the following three subsections.

c. Train Location of Mercury Deposits

The recovery and analysis of the M29 probe, filter, nitric acid impingers, sulfuric acid impingers and the hydrochloric acid rinse were kept separate for both the May 2001 and May 2002 M29 tests. The results are summarized and compared in Table C2. It is interesting to note that during the 2001 testing, only about 1% of the mercury was deposited on the quartz fiber filter. This is typical of most stack measurements of mercury, and as such there is little concern for the stability of the PM deposited on the filter. However, this is not the case for the 2002 mercury measurements. During these latter tests, 18% of the mercury was deposited on the filter during runs 1 through 5 with no lead in the mercury-nickel-zinc spiking solution. After adding lead to the spiking solution, the percent of mercury depositing on the filter increased to 29% for the remaining M29 runs.

Table C2. Comparison of the Location in M29 Sampling Trains Where the Mercury Was Deposited During the 2001 and 2002 Tests.

	YEAR	RUNS	FILT.	PROBE	M2B	M3A	M3B	M3C	TOTAL
Percent on Filter	2001	1-13	1.1	0.1	93	0.4	0.3	5.2	100
	2002	1-12	24.7	0.1	71	0.2	0.1	4.1	100
	2002	1-5	18.2	0.2	77	0.3	0.1	4.7	100
	2002	6-12	29.4	0.1	67	0.2	0.0	3.7	100
Mass on Filter (µg)	2001	1-13	6.0	0.2	414	2.2	1.0	26	450
	2002	1-12	166	0.8	484	1.6	0.4	28	681
	2002	1-5	129	1.1	551	1.9	0.7	34	718
	2002	6-12	191	0.6	437	1.4	0.2	24	654

It is interesting to note that during the 2001 M29 tests, the reported M29 mercury concentrations were 12% greater than the predicted concentrations; similar to the 18% (12% with corrected solution concentrations) measured this year with the XCEM. On the other hand, the 2002 M29 results are 6% less than the predicted concentrations rather than 12% greater like last year.

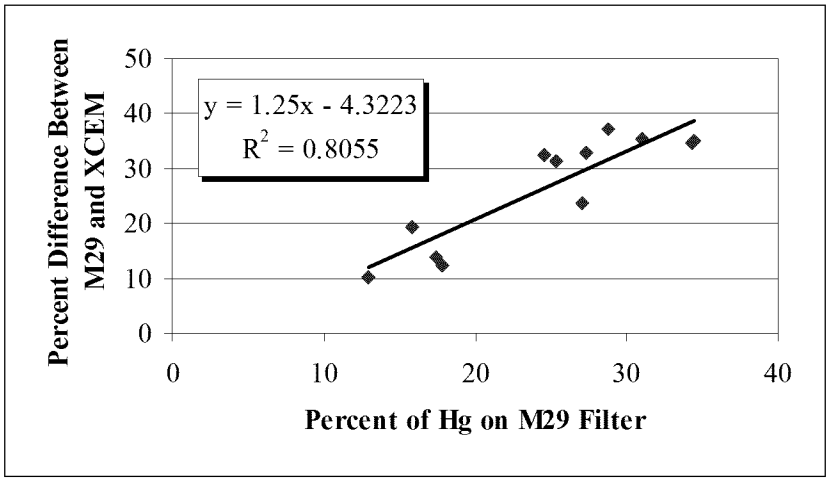
These results are certainly consistent with the hypothesis that M29 mercury results are low because there was a loss of mercury from the M29 quartz fiber filter between the time it was collected on the filter and the time it was analyzed. It is also consistent with the fact that many of the mercury compounds and amalgams of mercury are relatively unstable and have relatively high vapor pressures. Thus, it should not be surprising that

if there is a substantial portion of the mercury on the filter as there was during the 2002 tests, there might be a potential for significant loss due to volatilization. It also needs to be noted that the filters were not stored in a controlled environment from the time they were collected until they were delivered to the analytical laboratory several days later. During this time, they may have been exposed to relatively high ambient temperatures while being transported through the western desert from Tooele, UT to California in the back of a closed panel truck.

d. Correlation with Percent Mercury on M29 Filter

The percent difference between the M29 mercury results and the XCEM results is significantly correlated with the percent mercury on the M29 filters as is illustrated in Figure C2. That is, the percent difference between the two methods (percent loss from the M29 filter) is dependent on the fraction of the total mercury measured in the M29 train that is on the filter. This observation is consistent with the proposed hypothesis for the difference between the various methods, that is loss of mercury from the M29 filter.

Figure C2. Percent Difference Between M29 and the XCEM vs. Percent of Mercury on the M29 Filter



ii. Precision

The difference in the mercury concentrations was not likely due to imprecision in either of the two measurements. Mercury was one of two elements spiked by MSE-TA which were clearly not present in the background stack emissions. Thus, the variability in the mercury concentration was due primarily to variability in the spiking and stack flow rates. The mercury precision as measured by the XCEM was 3.8% and 6.1% for M29, which includes the variability in the above two parameters as well as the measurement method variability.

iii. Mercury to Nickel Ratio

Nickel was another element that clearly was not present in the background, and it was in the same spiking solution as the mercury. Thus, the ratio of mercury should not vary significantly since the concentrations for these two elements was kept constant for these latest tests. The XCEM measured mercury to nickel ratio was 1.37 ± 0.015 (1.1% relative) and close to both the M29 ratio, 1.41 ± 0.116 (8.3 % relative), and the predicted concentration ratio based on the measured solution concentration ratio of 1.33. It is interesting to note that the XCEM precision is significantly better than the M29 ratio precision, both of which should be relatively independent of factors other than the individual method.

iv. Low Columbia Analytical Services Results

The XCEM deposit samples submitted to Columbia Analytical Services for CVAA analysis were extracted 41 days after they were analyzed by CES. Based on an assumed linear loss rate, the expected mercury concentrations at the time of extraction would be about 10% lower than measured by the CES XRF analyzer. The observed difference was 14%.

4. CONCLUSION

The weight of evidence clearly indicates that the XCEM mercury deposit was unstable as well as the M29 PM deposit on the quartz fiber filter. This instability was most likely the cause of the difference between the mercury measured by these two methods and the other methods. It is highly likely that if these losses had not occurred, the XCEM would have passed the PS10 relative accuracy tests.

It is recommended that in future M29 testing, the filters be immediately sealed and cooled to at least 0°C, stored at below freezing temperatures and digested as soon as possible after sampling.