QUALITY ASSURANCE SUMMARY FOR MONTANA TEST OF CES's CEM

1.0. INTRODUCTION

Cooper Environmental Service's (CES) **X**-ray-based **C**ontinuous **E**missions **M**onitor (XCEM) extracted an isokinetic sample from the test duct through a one-inch diameter nozzle. This stack gas sample was slowed in a downward-flow stilling chamber where a second isokinetic sample was drawn through a test filter tape that trapped both particulate and ionic vapor-phase elements. The entire sample extraction system was heated to about 350°F. The sample analyzed by the X-ray fluorescence analysis part of the XCEM consisted of a spot with a diameter of about 0.25 inch, which was positioned near the center of the X-ray excitation beam.

There are two parameters (elemental mass and volume) that go into the calculation of stack gas concentrations, but there are four categories for potential errors in this measurement: sample extraction efficiency, filter sampling efficiency, elemental mass determination, and measurement of stack gas volume sampled.

Sample Extraction. The sample extraction system was designed to minimize loss of particulate due to impaction and settling. The use of a one-inch diameter nozzle made the extraction system relatively insensitive to flow variations. The stilling chamber was three inches in diameter and three feet long. The stilling chamber meets the eight diameter rule and previous tests of a similar stilling chamber has shown that the particle concentration at the test sample extraction point is uniform to within ±3%. Although there is bound to be some loss of particles and gaseous species to the walls of any extractive CEM, these losses can be minimized and the results adjusted for these small losses. In this particular test, the particulate losses prior to filter sampling appear to be less than about 10%. This estimate is based on the following reasons:

- Only about 10% of the Method 29 metals were deposited in the much smaller Method 29 nozzle and transport tubing.
- The average reported lead and chromium concentrations are 8% and 11%, respectively, less than the Method 29 concentrations. The arsenic, cadmium, chromium and lead concentrations after adjusting for calibration errors are only a couple of percent lower than the corresponding Method 29 results. Assuming similar particle size distributions for the other elements, it is unlikely that particle loss in the XCEM extraction component is a significant source of error.

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- The average reported lead and chromium concentrations are 8% and 11%, respectively, less than the Method 29 concentrations. The arsenic, cadmium, chromium and lead concentrations after adjusting for calibration errors are only a couple of percent lower than the corresponding Method 29 results. Assuming similar particle size distributions for the other elements, it is unlikely that particle loss in the XCEM extraction component is a significant source of error.

- The potential loss of gaseous species is expected to be low because the addition of chlorine gas resulted in the increase in only lead, and then only about one microgram. If other potential vapor phase species had been lost to the walls, the high temperatures and chlorine gas is expected to indicate this as it did with the small amount of lead.

Filter Sampling Efficiency. The filter sampling efficiency has been determined in the laboratory to be on the order of 98% for particulate and ionic vapor phase elements. Elemental vapors such as mercury have trapping efficiencies of less than 1%. The original test plan called for the addition of chlorine gas to convert the elemental mercury to mercuric chloride, which would then be trapped by the filter. Because of system problems, chlorine gas was used only for a few samples. Thus, the XCEM low reported mercury results are expected to be due to the presence of elemental mercury and its poor sampling efficiency. The Method 29 results suggest that the other metals were dominated by particulate species. Thus, the sampling efficiency is not expected to have contributed to differences in the XCEM and Method 29 results.

Elemental-Mass Determination. The elemental mass in the filter deposit was determined using an energy-dispersive X-ray fluorescence analyzer. This method is a particularly powerful tool for this application because the analysis is non-destructive and its results are potentially National Institute of Standards and Testing (NIST) traceable. In addition, the spectral results for each analysis are recorded, all of the elements are determined simultaneously, the elemental sensitivities are a smoothly varying function of atomic number, and the elemental analyzer is extremely stable, typically requiring recalibration only about once or twice a year. In this particular evaluation, the instrument was calibrated prior to the field tests, but the calibration could not be validated before the tests because of limited time. However, post calibration tests were conducted and indicated less than a 3% change in the calibration. Additional post calibration tests did indicate a bias in the XCEM calibration factors, which can explain most of the difference in the reported XCEM and Method 29 concentrations for arsenic, cadmium, chromium and lead concentrations. If the independent laboratory based XCEM calibrations factors are used, arsenic, cadmium, chromium and lead would all meet the EPA relative accuracy criteria of 20%. These adjustments are discussed in Section 4.0.

Volume Sampled. The volume of stack gas sampled was determined by subtracting the dilution gas volume from the total sample volume determined by a NIST-traceable mass flow meter. In the early part of the tests, the dilution volume was estimated with a rotameter, which was subsequently calibrated against the mass flow meter. In the latter portion of the tests, a second mass flow meter was used to determine the dilution gas used.

In general, uncertainties in the stack gas volume sampled are not expected to have contributed significantly to any of the differences in the Method 29 and XCEM

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In general, uncertainties in the stack gas volume sampled are not expected to have contributed significantly to any of the differences in the Method 29 and XCEM

results. This is based on the fact that the same volume is used in the calculations for each of the elements. Since the chromium and lead were very close to the Method 29 results, the volume used in the calculations for all the elements could not be significantly in error with either of the two methods.

2.0. PRE-TEST LABORATORY DETERMINATIONS

2.1. Energy calibration

The X-ray fluorescence analyzer component of the XCEM is periodically calibrated for energy. During this evaluation, the instrument was calibrated for energy prior to calibrations, and the online field tests.

2.2. Determination of elemental line interferences

Elements expected to be present in the test stack gas were determined from filter samples collected at the test facility. The analyzer was calibrated for these elements and potential spectral interferences determined. The elements present in the stack gas during the tests were as determined from the pre-test samples.

2.2. Blank interference and variability determinations

Blank filter tape elemental concentrations were determined prior to the tests and during the online field tests. In no case, was there a measurable amount of the reported elements present in the blank tape, nor was there a significant amount of a potentially interfering element. The only major elements present were sulfur and chlorine. The only measurable trace element impurities were a few nanograms per cm^2 of iron, zinc and bromine.

2.3. Elemental sensitivity determination

The analyzer elemental sensitivities or calibration factors were determined using thin-film standards (Micromatter), which are NIST traceable through gravimetric standards. These standards were internally evaluated by plotting elemental sensitivities versus atomic number. Because the electron binding energies and probabilities for creating electron vacancies is a smoothly vary function of atomic number, any elemental sensitivity falling off a best-fit smoothly varying curve was considered suspect and evaluated. The calibration factors used to calculate the originally reported results were based on these thin film standards. These factors were subsequently adjusted based on post analysis of XCEM spots by an independent analytical laboratory as discussed in Section 4.0.

Mercury was an exception to this procedure. Thin film mercury standards are not available. For these tests, a secondary mercury sample was used for spectral response calibration and a theoretical instrument ratio to lead was used to calculate a mercury intensity calibration factor. The instruments manufacturers theoretical ratio of 0.85 was used. This ratio has not yet been validated, and may be a source of some of the differences in the XCEM-reported results.

3.0. PRE-TEST ONLINE QUALITY ASSURANCE TESTS

3.1 Energy calibration

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3.1 Energy calibration

The XCEM was energy calibrated prior to the tests after it had been installed in the test facility. This energy calibration was checked periodically during the test period.

3.2 Elemental sensitivity check

The elemental sensitivity or calibration factors were checked at the site after system installation and just prior to the test runs by analyzing the thin film calibration standards as unknowns. The resulting XCEM results are compared to post-tests XCEM results in the following section. This comparison shows that instrument calibration drift was less than 3% between the online field application and post-test laboratory measurements over a month after the field tests.

4.0. POST TEST LABORATORY QUALITY ASSURANCE TESTS

The XCEM was disassembled after the online field tests and reassembled at CES's laboratory several weeks later. Several post-test quality assurance checks were conducted at this time. The results of these post quality assurance tests are discussed in the following subsections.

4.1. Energy calibration check

The system was calibrated for energy prior to instrument use to assure proper peak shape and location in the recorded X-ray spectra.

4.2. XCEM analysis of thin film standards as unknown

Thin film standards were used to calibrate the XCEM prior to online analysis. These same thin film standards were run again as unknowns prior to the online tests assuming a sample volume of 0.01 m^3. After the XCEM was returned to the laboratory, these thin film standards were again analyzed as unknowns as a post calibration check. The pre-test and post-test equivalent stack gas concentrations reported by the XCEM are compared below.

Element	In-field Pre-test results µg/m3	In-lab Post-test results µg/m3	Difference µg/m3	Percent
Sb	2541	2515	26	1.0
Pb	3108	3056	52	1.7
As	2044	2003	41	2.0
Cd	1510	1550	-40	-2.6

Clearly, there had not been a significant change in the XCEM calibration since the system was in use at the Montana tests and reassembled at CES's laboratory. This is important because the subsequent laboratory tests and potential

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adjustments of the field data rely on this determination that there has been no change in the elemental calibration factors since the online field tests.

4.3. XCEM reanalysis of selected XCEM field test samples

Seven XCEM deposit spots from the online field tests were reanalyzed in CES's laboratory. This was done to validate the online field test results and to assure the deposits had not lost a significant amount of mass when they came in contact with tape on the spool. The results of the laboratory analyses are compared with the online field test results in Table 1. The average difference between the laboratory and field measurements was 1.9%, with the laboratory results generally less than the field test results. This confirms the field measurements to an uncertainty of about 6% and suggests that possible loss of deposit mass was reasonably small. Four of these spots were submitted to Chester LabNet for GFAA (graphite furnace atomic absorption) analysis of arsenic, lead and cadmium (There was insufficient sample to analyze for antimony and chromium.), and two additional deposit spots were analyzed by CVAA (cold vapor atomic absorption) for mercury. The results from these analyses are discussed in the following subsection.

4.4. AAGF/CVAA analysis of selected XCEM field test samples

The seven selected deposit spots analyzed above were submitted to an independent laboratory (Chester LabNet) for wet-chemical analysis. Because of the small deposit mass, all of the reported elements could not be analyzed in each of the spots as noted above.

The results of post-test wet chemical analyses of the selected deposit spots from the field tests are summarized in Table 2. This table shows that there is no significant difference in the lead concentrations measured by the independent laboratory and measured at CES's laboratory. There was, however, significant differences in the two laboratory results for Hg, As, and Cd. The average difference for two mercury spots was 28%. This suggests that the mercury reported by the XCEM was low by, on average, 28%. This is not necessarily surprising since a theoretical sensitivity factor was used because of the absence of available mercury standards. The mercury results, however, would still be low relative to Method 29 results even with a 28% adjustment because of the low filter trapping efficiency for elemental mercury.

In the case of cadmium, the average difference in the laboratory XCEM results and the independent laboratory reported cadmium results is 17%. If the independent laboratory results were assumed to be the best representation of the true cadmium mass, the online XCEM calibration factor and field results would need to be increased by 17 %. With this adjustment, the average XCEM field test cadmium results would be in good agreement with the Method 29 cadmium results; that is, 98 $\mu g/m^3$ versus 100 $\mu g/m^3$.

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The independent laboratory arsenic results also suggest an average XCEM calibration bias of 24%. Again, if the independent laboratory results assumed to be the best representation of the arsenic mass in the XCEM spot, the XCEM arsenic calibration factor and field results would need to be increased by 24%. Again, with this adjustment, the average XCEM arsenic results are in good agreement with the method 29 results, 25 $\mu g/m^3$ for Method 29 versus 21 $\mu g/m^3$ for the XCEM.

The good agreement for the independent laboratory and XCEM laboratory lead results is strongly supportive of the online field XCEM results. The XCEM results would be a couple of percent closer in agreement with the Method 29 results if the independent laboratory lead results were used to adjust the XCEM calibration factor for lead. With this adjustment, the average XCEM lead is 67 $\mu g/m^3$ compared to 70 $\mu g/m^3$ for Method 29.

The antimony results, however, differ by more than five fold. There was insufficient sample available for the determination of chromium and antimony on the spots submitted for independent analysis. However, it is clear at this time that the reported Method 29 antimony results are grossly in error and probably due to poor recovery of antimony in the analytical laboratory. This conclusion is based on the generally good agreement between the two methods (after adjusting calibration factors) for arsenic, cadmium, chromium and lead, the higher XCEM results, and the XCEM measured antimony to cadmium ratio. The good agreement for these four elements strongly validates the volumes used in both methods. Thus, the antimony difference cannot be explained by a difference in the volumes used to calculate the antimony concentration.

The fact that the XCEM results are about six-fold greater than the Method 29 results implies that the difference is not due to loss of antimony in the XCEM. However, there is a well-established potential for loss of antimony in some EPA filter digestion procedures such as EPA Method 3050, SW 846.

In addition, the XCEM results show that the antimony stack gas concentration is clearly almost two times greater than the cadmium concentration, not almost six times less than the cadmium concentration as suggested by the Method 29 results. Since the cadmium results are in good agreement, the difference in the elemental ratio must be associated with the antimony. Because the XCEM measures the antimony and cadmium simultaneously, its measure of the ratio is highly reliable and expected to have an uncertainty of no more than about 10%. In addition, since the spectra for each sample spot was saved, they were reviewed and the analyte line intensities and reported relative concentrations were confirmed.

Additional spots have been submitted to an independent laboratory for antimony and cadmium determinations. These results will contribute significantly to our understanding of the differences in reported antimony results

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Thus, for the above stated reasons, it is highly likely that the Method 29 results are in error due to loss of antimony, most likely through either volatilization or in the filtered precipitate prior to instrumental analysis.

It is also important to note that this type of post-independent laboratory analysis is possible because of the nondestructive nature of the XCEM analysis and the above-demonstrated minimal loss of deposit to other portions of the tape on the spool. The comparison of results is essentially equivalent to a pre-analysis spike recovery test. The primary limitation of this type of post-test analysis recovery evaluation is the analytical sensitivity and accuracy of the method used by the independent laboratory.

4.5. XCEM analysis of spikes

In addition to the above quality assurance steps, a post-test analysis of spiked filter samples was conducted. The resulting calibration factors using spikes for arsenic, cadmium, lead and antimony are generally supportive of the above conclusions.

Table 1. Comparison of Online Field Test Results with Post-Test Lab Results

Overall XRF Run	12/9/99 Run No.	CES Lab	Field	% Diff	CES Lab	Field	% Diff	CES Lab	Field	% Diff
		CR	CR	CR	HG	HG	HG	AS	AS	AS
64	39	34.0	34.4	-0.9	19.4	21.3	-9.4	22.3	15.4	36.3
65	40	32.7	37.7	-14.2	20.6	20.8	-0.9	23.5	25.7	-8.8
66	41	36.4	31.6	14.2	19.7	20.5	-3.9	22.2	19.8	11.5
67	42	36.5	36.7	-0.5	19.9	23.2	-15.1	22.4	18.5	18.9
68	43	30.4	31.2	-2.5	18.9	18.7	1.4	18.7	20.4	-8.6
69	44	31.9	28.7	10.6	15.7	20.8	-28.3	21.9	18.6	16.1
Average		**33.7**	**33.4**	**1.1**	**19.0**	**20.9**	**-9.4**	**21.8**	**19.8**	**10.9**

Overall XRF Run	12/9/99 Run No.	CES Lab	Field	% Diff	CES Lab	Field	% Diff	CES Lab	Field	% Diff
		PB	PB	PB	CD	CD	CD	SB	SB	SB
64	39	98.1	95.2	3.0	109	118	-8.0	197	211	-6.9
65	40	98.0	108.2	-9.9	110	118	-7.5	208	211	-1.2
66	41	96.1	101.4	-5.4	106	105	0.5	193	188	2.9
67	42	97.9	114.1	-15.3	111	111	-0.2	211	196	7.3
68	43	87.2	97.6	-11.2	97	104	-7.3	188	205	-8.4
69	44	86.0	92.5	-7.3	94	95	-0.5	169	185	-9.3
Average		**93.9**	**101.5**	**-7.7**	**104.4**	**108.6**	**-3.9**	**194.3**	**199.2**	**-2.6**

Thus, for the above stated reasons, it is highly likely that the Method 29 results are in error due to loss of antimony, most likely through either volatilization or in the filtered precipitate prior to instrumental analysis.

It is also important to note that this type of post-independent laboratory analysis is possible because of the nondestructive nature of the XCEM analysis and the above-demonstrated minimal loss of deposit to other portions of the tape on the spool. The comparison of results is essentially equivalent to a pre-analysis spike recovery test. The primary limitation of this type of post-test analysis recovery evaluation is the analytical sensitivity and accuracy of the method used by the independent laboratory.

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68	43	30.4	31.2	-2.5	18.9	18.7	1.4	18.7	20.4	-8.6
69	44	31.9	28.7	10.6	15.7	20.8	-28.3	21.9	18.6	16.1
Average		**33.7**	**33.4**	**1.1**	**19.0**	**20.9**	**-9.4**	**21.8**	**19.8**	**10.9**

Overall XRF Run	12/9/99 Run No.	CES Lab	Field	% Diff	CES Lab	Field	% Diff	CES Lab	Field	% Diff
		PB	PB	PB	CD	CD	CD	SB	SB	SB
64	39	98.1	95.2	3.0	109	118	-8.0	197	211	-6.9
65	40	98.0	108.2	-9.9	110	118	-7.5	208	211	-1.2
66	41	96.1	101.4	-5.4	106	105	0.5	193	188	2.9
67	42	97.9	114.1	-15.3	111	111	-0.2	211	196	7.3
68	43	87.2	97.6	-11.2	97	104	-7.3	188	205	-8.4
69	44	86.0	92.5	-7.3	94	95	-0.5	169	185	-9.3
Average		**93.9**	**101.5**	**-7.7**	**104.4**	**108.6**	**-3.9**	**194.3**	**199.2**	**-2.6**

Table 2. Comparison of XCEM Results (In CES lab) With Independent Lab Results

Run	As			Cd			Pb			Hg		
	XCEM[a]	AA[b]	% Diff.	XCEM[a]	AA[b]	% Diff.	XCEM[a]	AA[b]	% Diff.	XCEM[a]	AA[b]	% Diff.
63										24	35	33
64	15	23	32	118	143	18	95	100	4			
65	26	30	16	118	140	16	108	108	0			
66	20	25	20	105	129	18	101	103	2			
67	19	21	12	111	130	14	114	111	-3			
68	20	35	41	104	125	17	97	105	7			
69										24	31	23
Mean	20	27	24	111	133	17	103	106	2	24	33	28
SD	4	6	12	7	8	2	8	4	4	0	3	7
Range	15-26	23-35		104-118	125-143		95-108	100-111		24	31-35	

a) Reported final corrected concentrations

b) Concentrations based on elemental mass determination by GFAA for As, Cd and Pb, and CVAA for Hg

Table 2. Comparison of XCEM Results (In CES lab) With Independent Lab Results

Run	As			Cd			Pb			Hg		
	XCEM[a]	AA[b]	% Diff.	XCEM[a]	AA[b]	% Diff.	XCEM[a]	AA[b]	% Diff.	XCEM[a]	AA[b]	% Diff.
63										24	35	33
64	15	23	32	118	143	18	95	100	4			
65	26	30	16	118	140	16	108	108	0			
66	20	25	20	105	129	18	101	103	2			
67	19	21	12	111	130	14	114	111	-3			
68	20	35	41	104	125	17	97	105	7			
69										24	31	23
Mean	20	27	24	111	133	17	103	106	2	24	33	28
SD	4	6	12	7	8	2	8	4	4	0	3	7
Range	15-26	23-35		104-118	125-143		95-108	100-111		24	31-35	

a) Reported final corrected concentrations

b) Concentrations based on elemental mass determination by GFAA for As, Cd and Pb, and CVAA for Hg