XCEM QA APPLIED TO EVALUATION OF XCEM/M29 MERCURY CONCENTRATION DIFFERENCES MEASURED DURING RELATIVE ACCURACY TESTS

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.

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.

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.

2. AA

a. 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.

3. AAA

a. 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.

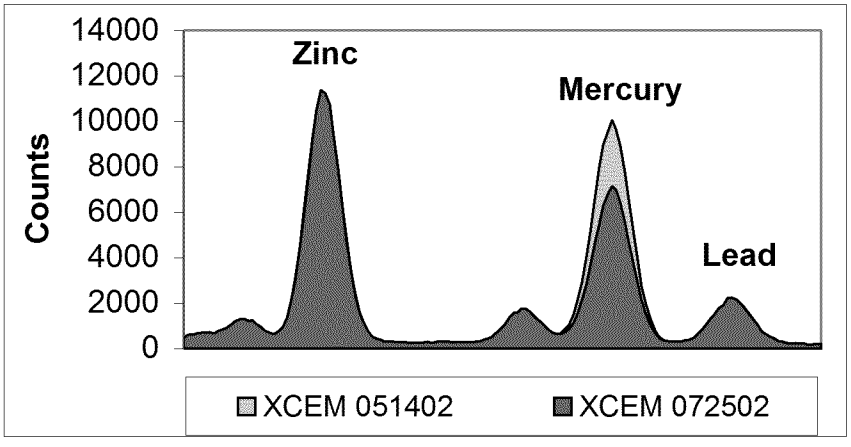
b. XCEM Measurements (XCEM)

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

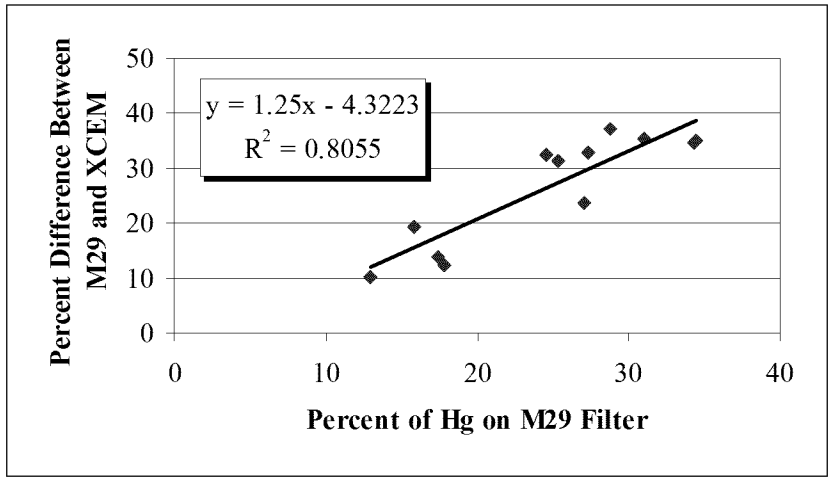
It is interesting to note that during the 2001 M29 tests, the reported M29 mercury concentrations were 12% greater than the predicted concentrations; similar to the 18% (12% with corrected solution concentrations) measured this year with the XCEM. On the other hand, the 2002 M29 results are 6% less than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

OTHER FACTORS THAT COULD CONTRIBUTE TO DIFFERENCES IN XCEM AND M29 MERCURY MEASUREMENTS

1. XCEM MEASUREMENTS
    a. Systematic Errors
        i. Impacting All Elements
            1. Volume
                a. Meter: Could contribute either a positive or negative artifact. Three NIST traceable meter/regulator compared well during test. Estimated uncertainty is 3% of the reported flow rate.
                b. Volume Adjustment: The calculated volume was adjusted by a factor of 1.025 (increased by 2.5%) to compensate for incomplete drying of the air, which was determined in CES's laboratory prior to shipping the XCEM. The uncertainty in this adjustment factor is estimated an ±0.020. Because of the actual conditions during the testing at the Army incinerator, it is thought that this adjustment is possibly too large for the actual incinerator conditions. Thus, it is possible that the recorded concentrations reported by the XCEM were high by 1 to 2% due to this adjustment factor.
                c. Leak: This source of error would contribute a negative artifact to the XCEM results. The XCEM results were greater than the M29 results. As such, this source of error could not explain the observed difference. In addition, the pressure drop across the filter is monitored during the testing and recorded in the system. No alarms were noted and none were indicated upon review of the data. This source of possible error is expected to contribute well less than 1% to the uncertainty in the flow measurement.

            2. Thin Film to Spot Calibration Factor
                a.
            3. Deposit Positioning (XYZ)

a. Direction of tape flow (X): The accuracy of tape movement in this direction is ±0.025 mm. The XRF beam intensity is insensitive to deposit spot position in this direction to ± 1mm. The uncertainty in concentration due to positioning error in this direction is expected to be substantially less than 1%. This error would bias the results low because it would tend to place the deposit at a non-optimal position.
b. Perpendicular to tape flow direction and in the same plain (Y): The large axis of the X-ray beam is aligned in this direction. As such, the XCEM is less sensitive to deposit positioning in this direction. The alignment of the sampling plunger and the analysis beam spot are accurate to ±0.050 mm. The XRF beam intensity is insensitive to deposit spot position in the Y direction to ±1.5 mm. Misalignment of the tape has no impact on the intensity as long as the spot is on the tape. Thus, error in the alignment of the deposit and analysis position in this direction is expected to be insignificant; i.e., substantially less than 1%. This error would bias the results low because it would tend to place the deposit at a non-optimal position.
c. Height of tape above tube and detector (Z): Differences between the tape deposit and calibration standards position in the Z direction can contribute systematic error to all of the elements. It is not subject to error in the X and Y directions because the standards are larger than the analysis spot. The XCEM has been designed to position the tape deposit in the middle of the XRF analysis plain. In this position, the beam is relative insensitive to position in the Z direction at the ±0.1 mm range. The error due to differences in position of the tape deposits and the standards has been empirically determined to be less than 0.5% at the 95% confidence level. In this case, the results could be biased either high or low.
d. Shape of deposit: Misalignment of the XCEM plunger and the supporting button can cause deviations from a circular deposit. In general, the XRF intensity is insensitive to deposit geometry so long as the spot is smaller than the beam diameter. However, because there are small variations in sensitivity within the beam area, error can be

introduced due to variations in deposit geometry. It has been empirically determined that there is less than a 3% difference in sensitivity for a deposit the size of the XCEM deposit, 6 mm diameter, and a 3 mm diameter spot (one fourth the area). From observation of the small deviations of spot geometry for actual deposits during these tests, it is estimated that this source would contribute no more than about 1% uncertainty to the reported XCEM results. These deviations, however, would be such that it would bias the XCEM results high.

ii. Impacting One or More Elements

1. Transport
   a. Hg
   b. PM
   c. Hg/Ni
2. Calibration Errors
   a. Uncertainty in Standard Concentration
      i. Stated Concentrations
      ii. Sensitivity Curves
   b.
3. Spectral Analysis
   a. Energy calibration
4. Analyte Line Interferences
   a. Zn and Pb on Hg
   b. Ba on Cr
   c. Pb on As
5. Background/Blank Interferences
   a. Cr
6. aa
7.

b. Random Errors

i. Impacting All elements

1. Tape positioning
2. **Tape Efficiency**

ii. Impacting One of More Elements

1. Contamination
2. Counting Statistics
3. Signal to Noise

c. Quality Assurance and Control Measures During Tests

i. XCEM Stability: The stability of the XRF component of the XCEM was monitored with each analysis, using Pd peak intensity from a Pd rod permanently positioned in the X-ray beam. This intensity varied from 95% to 105% of the mean during the M29 tests compared. Counting statistics was responsible for most of this variability, and no drift trends were apparent.

ii. Daily Zero and Span Checks: The XCEM has the capability for automated zero and span checks. These were not conducted during this series of tests. Instead, measurements of NIST and Army standards were made at the beginning and end of each day of testing.

iii. NIST and Army Standard Measurements

1. NIST standards (SRM 1832 and 1833) were analyzed daily during the tests. They were usually run before and after each days runs. Recovery for Ti, V, Mn, Fe, Cu, Zn, and Pb were 100±2% of the NIST value. Thin film NIST standards for Cr, Ni, As, Cd, Sn, Sb, Ba and Hg are not available. Hg was calibrated using its relationship to Pb and other L-line standards, and its stability was checked using a HgAg standard, which gave replicate analysis results to within ±3%.
2. The other non-NIST standard elements were checked with Army secondary standards calibrated at CES laboratories. Repeated measurements with these standards yielded recoveries of 100±3%.

iv. Energy Calibration: The XRF analyzer component of the XCEM was calibrated each morning to minimize impacts of small drifts in peak position. Errors associated with peak drift would be exhibited in standard replication, which was typically less than ±3%.

d. Summary of Potential XCEM Errors
e. Aa
f.

2. METHOD 29 MEASUREMENTS
   a. M29 Train Replication
   b. Velocity
   c. Loss
   d. Contamination
   e. Laboratory Analysis
   f. Recovery Efficiency
3. AAA

5. 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.