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Construction Engineering Research Laboratory

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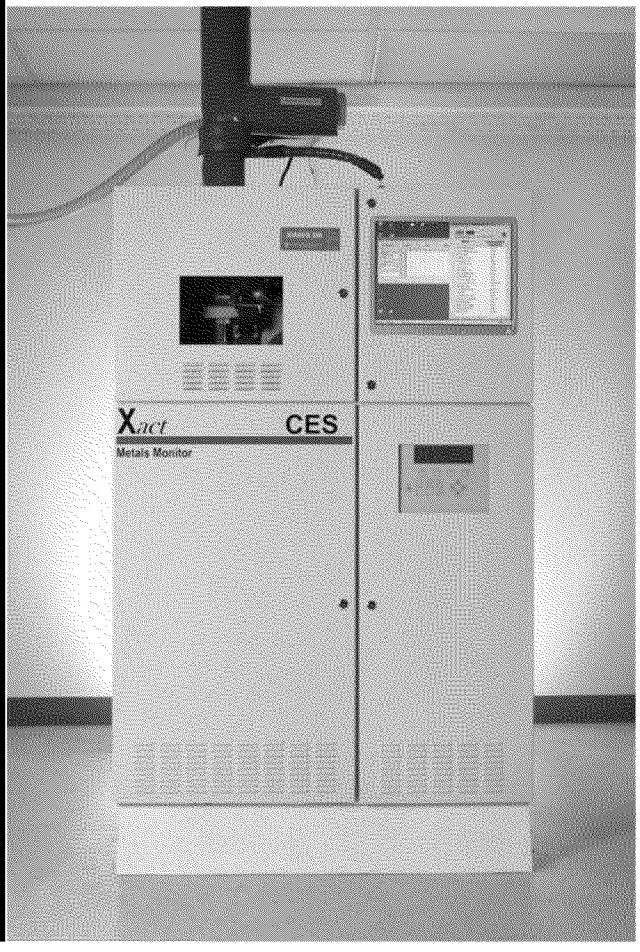
Engineer Research and Development Center

X-Ray Fluorescence-Based Multi-Metal Continuous Emission Monitor

Technology Demonstration

K. James Hay, Veera M. Boddu,
Bruce E. Johnsen, and John A. Cooper

March 2005



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X-Ray Fluorescence Based Multi-Metal Continuous Emission Monitor: Technology Demonstration

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Final Report

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ABSTRACT: Army demilitarization incinerators will need to comply with the Hazardous Waste Combustor National Emission Standard for Hazardous Air Pollutants that will regulate metals and metal compounds listed under the Clean Air Act Amendments. A large problem for these incinerator operations is limited knowledge of the type and quantity of emitted metals, so that compliance may be determined only through trial burn emission tests. A continuous emission monitor (CEM) for multi-metals will provide the emission data, a tool to help meet compliance requirements, and the opportunity to adjust burn strategies for increased production. A user-friendly multi-metal CEM that uses x-ray fluorescence (XRF) as the analytical method and an automated sampling system that provides extractive batch sampling onto a filter tape (XCEM) was demonstrated at the 1236 Deactivation Furnace at Tooele Army Depot, Utah. The unit was compared to EPA Reference Method 29 during two separate tests (2001 and 2002). The second test was performed after improvements were made to the sample transport and system calibrations. The results indicate that the XCEM has met the proposed Performance Specification 10 for multi-metal CEMs except for relative accuracy requirements for 4 of 9 metals. Its failures are attributed mostly to inadequacies in the reference method. The monitor is proving useful at Tooele and is ready for implementation at other Army demilitarization incinerators.

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R5-2014-0104710000365

Contents

List of Figures and Tables v

Conversion Factors vii

Preface viii

1 Introduction 1

Background 1

Objective 3

Approach 4

Mode of Technology Transfer 4

2 Field Testing 2001 5

Brief Description of XCEM 5

Extraction System 5

Sampling and Analysis System 6

Control System 7

Execution of Field-Testing Activities 7

Test Plan 8

EPA Verification 9

TEAD Interface 9

Test Objectives 10

Site Description 11

Experimental Design 14

Results 15

XCEM Reported Concentrations 15

Sampling and Response Time 19

Zero and Calibration Drift 19

Correlation with Reference Method 20

Response to Changes in Metal Concentration 25

Relative Accuracy 25

Precision 33

Low-Level Metal Response 35

Bias 36

Summary 37

R5-2014-0104710000365

3 Transport and Calibration Improvements....39

Transport Line Changes....39

Recalibration....40

Summary of Transport and Calibration Evaluations....40

4 M29 Comparison Testing of XCEM 2002....42

Results....42

Method 29 Concentrations....42

Predicted Stack Gas Concentrations....43

XCEM Concentrations....47

XCEM Calibration Evaluation Using A QuanX – XRF and ICP/MS....53

Precision....53

Discussion....54

Regulated Elements Typically Found in the Feedstream....54

Regulated Elements Not Typically Found in TEAD Emissions....58

Nonregulated Metals....63

Summary....63

5 XCEM Cost and Status....65

Cost Estimates....65

Capital Costs....65

Annual Costs....66

Continued Use of the XCEM....66

6 Summary and Conclusions....68

References....71

Appendix A: Test/QA Plan for Verification of a Continuous Emission Monitor for Multi-metals at Tooele Army Depot (2001)....73

Appendix B: Determination of XCEM Reported Concentrations 2001....101

Appendix C: Transport and Calibration Evaluations....106

Appendix D: Mercury Calibration and Loss Discussion 2002....117

Abbreviations and Acronyms....125

Report Documentation Page....127

R5-2014-0104710000365

List of Figures and Tables

Figures

1 XCEM stilling chamber and sampling cassette 6

2 XCEM chassis 7

3 New Component Control Screen for XCEM software interface 8

4 XCEM housing and transport line, M29 sampling setup, stack, and ceramic baghouse at TEAD 10

5 TEAD incinerator setup and sampling/spiking locations 13

6 Spiking at base of stack during validation testing 15

7 Palladium concentrations during M29 testing 21

8 XCEM and M29 concentrations during TEAD verification testing 22

9 Correlation between XCEM and M29 for elements spiked at two levels 24

10 XCEM and M29 lead concentrations during runs 8–11 28

11 Ratio of XCEM to M29 concentrations during validation testing 30

12 Uncorrected XCEM As concentrations versus XCEM Pb concentrations 32

13 Correlation between Sn and other APE-1236 metals with munitions burning and no spiking 46

14 XCEM tin measurements during M29 testing 46

15 XCEM versus M29 lead for validation tests 56

16 Percent difference between M29 and the XCEM versus percent of Hg on M29 filter 60

17 2004 CES metals monitor 67

C1 Experimental design for atomization tests 107

C2 XCEM reported concentrations for nonspiked elements 113

C3 XCEM reported concentrations and MSE-projected concentrations for spiked elements 114

D1 Comparison of XCEM x-ray spectra measured during M29 testing and 71 days later 121

D2 Percent difference between M29 and the XCEM vs. percent of Hg on the M29 filter 123

Tables

1 Army hazardous waste combustors....2
2 Proposed PS-10 requirements....3
3 XCEM test dates and associated TEAD incineration feedstream....9
4 Typical operating parameters for the APE-1236 deactivation furnace....12
5 TEAD metal emission limits during verification testing....12
6 TEAD incinerator metal emission limits and spiking levels....14
7 Final reported CEM concentrations for M29 testing....17
8 Upscale and zero concentrations during validation testing....20
9 Correlation between the XCEM and M29....25
10 XCEM measured, M29 measured, and MSE-predicted metal concentrations during TEAD validation testing....26
11 Relative accuracy and correlations....27
12 Percent differences between M29 sample trains....34
13 XCEM and M29 precision....35
14 Method 301 bias and correction factor comparison....37
15 Summary of XCEM performance relative to proposed PS-10 requirements....38
16 M29 concentrations....43
17 APE-1236 stack flow rates during M29 testing....44
18 APE-1236 stack concentrations with munitions incineration but no spiking....45
19 Predicted stack concentrations based on MSE-TA spiking and background estimates....47
20 XCEM concentrations....48
21 Analysis of XCEM filter tape by Columbia Analytical....53
22 Predicted (spiked), XCEM, and M29 precision during validation testing....53
23 TEAD emission limits for regulated elements....54
24 Summary of Pb concentration data and ratios during M29 testing....55
25 Summary of Cd concentration data and ratios during M29 testing....57
26 Summary of Cr concentration data and ratios during M29 testing....58
27 Summary of As concentration data and ratios during M29 testing....59
28 Summary of Hg concentration data and ratios during M29 testing....60
29 Summary of Sb concentration data and ratios during M29 testing....61
30 Summary of Ni concentration data and ratios during M29 testing....62
31 Summary of Ba concentration data during M29 testing....62
32 Summary of Zn concentration data and ratios during M29 testing....63
33 Summary of 2002 M29/XCEM comparison results....64

R5-2014-0104710000365

B1 Original XCEM reported concentrations uncorrected for calibration and dryer changes....103
B2 Results of dryer tests....105
C1 Flow rates and concentrations used to calculate atomization concentrations....109
C2 Atomization vs. XCEM concentrations....109
C3 Total capture mass vs. atomization mass....111
C4 Lead normalized atomization mass vs. total capture....111
C5 Method 17 vs. XCEM at TEAD....116
D1 Mercury reported concentrations during Year 2002 M29 validation testing....120
D2 Comparison of the location in M29 sampling trains where the Hg was deposited during the 2001 and 2002 tests....122

Conversion Factors

Non-SI* units of measurement used in this report can be converted to SI units as follows:

Multiply	By	To Obtain
degrees Fahrenheit	(5/9) x (°F – 32)	degrees Celsius

Système International d'Unités ("International System of Measurement"), commonly known as the "metric system."

R5-2014-0104710000365

Preface

This study was conducted for Headquarters, Department of the Army under Program Element 063728A, "Environmental Technology Demonstration"; Project 002, "Environmental Compliance Technology"; Work Unit CNE-B091, "Hazardous Air Pollutants Technology Demonstrations." The technical reviewer was Thomas Logan, U.S. Environmental Protection Agency.

The work was performed by the Environmental Process Branch (CN-E) of the Installations Division (CN), Construction Engineering Research Laboratory (CERL). The CERL Principal Investigator was Dr. K. James Hay. Part of this work was done by Cooper Environmental Services under DACA42-02-P-0072 and DACA42-01-C-0022; MSE Technology Applications, Inc. under GS-10F-0212K; and the U.S. Army Center for Health Promotion and Preventive Medicine. The technical editor was Linda L. Wheatley, Information Technology Laboratory — Champaign. Dr. Kirankumar V. Topudurti is Chief, CN-E, and Dr. John T. Bandy is Chief, CN. The associated Technical Director was Gary W. Schanche. The Director of CERL is Dr. Alan W. Moore.

CERL is an element of the U.S. Army Engineer Research and Development Center (ERDC), U.S. Army Corps of Engineers. The Commander and Executive Director of ERDC is COL James Rowan, and the Director of ERDC is Dr. James R. Houston.

R5-2014-0104710000365

1 Introduction

Background

The U.S. Environmental Protection Agency (EPA) is developing regulations for hazardous waste combustors (HWC) as part of Title III of the 1990 Clean Air Act Amendments (CAAA) in the form of a National Emission Standard for Hazardous Air Pollutants (NESHAP). The U.S. Army possesses a number of demilitarization furnaces that will need to comply with these regulations. Of most concern is meeting the requirements for metals and metal compounds listed under the CAAA. A large problem for these incinerator operations is limited knowledge of the types and quantities of emitted metals. Compliance may be determined only through trial burn emission tests because of this limitation. These tests are expensive and require worst-case scenario burns. The air permits that are then issued are based on these worst-case burns and impose limitations on the demilitarization facilities. A continuous emission monitor (CEM) for metals would provide the emission data, a tool to help meet compliance requirements, and the opportunity to adjust burn strategies for increased production and sustainability. In addition, the HWC NESHAP suggests that a CEM would be the preferential method of emission accountability.

Multi-metal CEMs being developed are based on elemental sensors using laser-induced breakdown spectroscopy (LIBS) or inductively coupled plasma (ICP). None of the LIBS monitors has successfully met the EPA-proposed Performance Specification 10 (PS-10; EPA 1996) for continuous multi-metal monitors. Only one of the ICP units, developed by Thermo Jarrell Ash Corporation, has been successful in meeting the relative accuracy (RA) criteria of the PS-10 (Seltzer 2000). This technology appears to have limitations such as its complexity, high initial costs, and high operating costs. The U.S. Army Engineer Research and Development Center, Construction Engineering Research Laboratory (ERDC/CERL) decided to pursue the development of the X-ray fluorescence (XRF)-based continuous emission monitor (XCEM) because it had the potential to be a reliable and accurate CEM without these limitations.

The basic approach of the XCEM is to draw a continuous representative sample of stack gas to a stilling chamber where a smaller metered sample is extracted and passed through a chemically treated filter that collects metals in the particu-

R5-2014-0104710000365

late and vapor phases. Following sampling, the filter is passed through an XRF analyzer where the masses of up to 19 metals are measured. This approach was originally tested in 1997 at an EPA test incinerator, where the filters were analyzed offline (French 1998). Cooper Environmental Services (CES) further developed this method into an on-line system that was tested under the ERDC/CERL Waste Minimization and Pollution Prevention Program at MSE Technology Applications, Inc.'s (MSE-TA's) research incinerator in Butte, Montana (Bryson et al. 2000). The results were encouraging because the XCEM met the PS-10 RA requirements for chromium (Cr) and lead (Pb). Many of the other requirements were unmet, however, and further development was needed. It was at this point that ERDC/CERL began funding the development of this technology under their Hazardous Air Pollutants (HAP) program.

The Army currently has 19 existing, new, or planned hazardous waste combustors. Table 1 lists these sites (Josephson 2003).

Table 1. Army hazardous waste combustors.

Location	Type	Waste Treated	Status	GO or CO
Sierra AD	APE 1236	CS	Existing	GO
Tooele AD	APE 1236	CS	Existing	GO
Tooele AD	APE 1236	Test Furnace – CS	Existing	GO
McAlester AAP	APE 1236	CS	Existing	GO
Hawthorne AAP	APE 2210	CS	New	CO
Fort Richardson	APE 1236	CS	New	GO
Kansas AAP	APE 1236	CS	Existing	CO
Crane AAP	APE 1236	CS	New	GO
Lake City AAP	APE 1236	Off-spec conventional	Existing	GO
Picatinny Arsenal	APE 1236	Waste R&D propellants	New	GO
Pine Bluff Arsenal	Fluidized Bed	Pyrotechnics and Obscurants	New	GO
Pine Bluff Arsenal	APE 1236	Off-spec pyrotechnics	Existing	GO
Radford AAP	Kiln	Off-spec propellants	Existing	GO
Deseret CA	Chemical	Chem	Existing	GO
Umatilla AD	Chemical	Chem	New	GO
Pine Bluff Arsenal	Chemical	Chem	New	GO
Anniston AD	Chemical	Chem	New	GO
Pueblo CA	Chemical	Chem	Planned	GO
Anniston AD	Kiln	De-Painting wastes	Planned	GO

GO – Government Owned
CS – Conventional Stockpile
AD – Army Depot
CO – Contractor Owned
Chem – Chemical Stockpile
AAP – Army Ammunition Plant
CA – Chemical Activity
APE - Ammunition Peculiar Equipment

R5-2014-0104710000365

Objective

The overall objective of the HAP program is to develop cost-effective technologies to help the Army meet current and future demands of HAP regulations. Toward this objective, the XCEM was developed. It was developed to possess characteristics that make it compatible with Army operations and expectations, such as user friendliness and affordability. That work is described in a precedent-setting report (Hay et al. 2005). The specific objective of this work was to demonstrate the XCEM at an Army installation. The desired exit criterion under the HAP Program was for the monitor to meet, under field conditions, the proposed PS-10 requirements, which are described in Table 2.

Table 2. Proposed PS-10 requirements.

Criterion	Description
Sampling and response time	It is required that the sampling time be no longer than one-third of the averaging period for the applicable standard for a batch CEM. The delay between the end of the sampling period and reporting of the sample analysis shall be no greater than 1 hour. A batch CEM is required to sample continuously except when changing the sampling media, which should be no greater than 5 percent of the averaging period or 5 minutes, whichever is less. For this study, the averaging period is 12 hours, which means the sampling time should be no longer than 240 minutes, the response time no greater than 60 minutes, and the maximum time allowed for changing the sampling media is 5 minutes.
Quality assurance	Calibration drift: The calibration may not drift or deviate from the reference value of the calibration standard used for each metal by more than 5 percent of the emission standard for each metal. Must allow for determining on a daily basis. Zero drift: The zero point for each metal shall not drift by more than 5 percent of the emission standard for that metal. Must allow for determining on a daily basis. Span: The CEM response range must include zero and a high level value equal to the span. The span value is defined as 20 times the applicable emission limit for each metal. This is an equipment specification (not tested).
RA	The RA of the CEM must be no greater than 20 percent of the mean value of the RM test data in terms of units of emission standard for each metal, or 10 percent of the applicable standard, whichever is greater. During verification, the measure of RA at a single concentration level is required for each metal measured for compliance purposes, and the RA must be determined at three concentration levels for one metal (zero can be one level).

Source: EPA 1996.

R5-2014-0104710000365

Approach

As a result of encouraging development work (Hay et al. 2005) a new monitor was installed at the 1236 production deactivation furnace at Tooele Army Depot (TEAD), Utah. The monitor was compared to EPA Reference Method 29 (M29) in 2001. The monitor was only partly successful; several improvements were warranted and implemented. A second M29 field-test was conducted a year later. This report includes the description and results from both M29 comparison tests and the modifications that took place in between. The XCEM was demonstrated under this project through contracts with CES and MSE-TA. The U.S. Army Center for Health Promotion and Preventive Medicine (CHPPM) performed the M29 stack sampling activities described in this report.

Mode of Technology Transfer

This technology was developed and demonstrated through the ERDC/CERL HAP Program, which uses 6.3 advanced development and field-testing funds. The HAP Program is part of the Army Environmental Quality Technology (EQT) Program. As part of the EQT process, a technology transfer plan is being developed by the Army Environmental Center (AEC) for this technology as well as other qualified technologies under the HAP program. A User's Guide and Resource Manual have been developed to accompany the XCEM for field training and reference (CES 2001a, 2001b). This technology is ready for transfer to Army facilities, and transition has already begun. The Army purchased another XCEM in 2003 for use at the 1236 Test Deactivation Furnace at TEAD.

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http://www.cecer.army.mil

R5-2014-0104710000365

2 Field Testing 2001

The XCEM underwent M29 comparison testing at the TEAD 1236 deactivation furnace in May 2001. This chapter presents a brief description of the XCEM, the testing activities, and the results of the testing.

Brief Description of XCEM

A new XCEM was developed and built for demonstration at the TEAD facility as described in Hay et al. (2005). The XCEM extracts a sample of stack gas and concentrates the metals of interest on a chemically treated filter tape. Following collection, the filter tape is advanced to an analysis area where a laboratory-grade XRF instrument is used to determine metal mass. The system is entirely automated and produces concentration data every 10 to 20 minutes for up to 19 elements of interest. The three major XCEM components are: an extraction system, sampling and analysis system, and control system.

Extraction System

The XCEM extraction system collects a representative stack gas sample from the smokestack and transports the sample to the filter. The system includes a sample probe and insulated sample line. The stack gas temperature is monitored in the sample line just before it enters the enclosure that houses the XCEM. The unit only operates when this temperature is above the dew point for water. Upon entering into the enclosure, the stack gas passes through a heat-traced stilling chamber with a larger diameter that slows the gas velocity (Figure 1). Approximately 1 percent of the stack gas that enters the stilling chamber is sampled through an extraction tube for concentration on a filter. The remaining 99 percent of the gas is transported out of the stilling chamber, through a flow meter, and vented or returned to the stack (2 to 3 standard cubic feet per minute, SCFM). An eductor, located downstream of the stilling chamber, is used to pull the stack gas through the extraction system.

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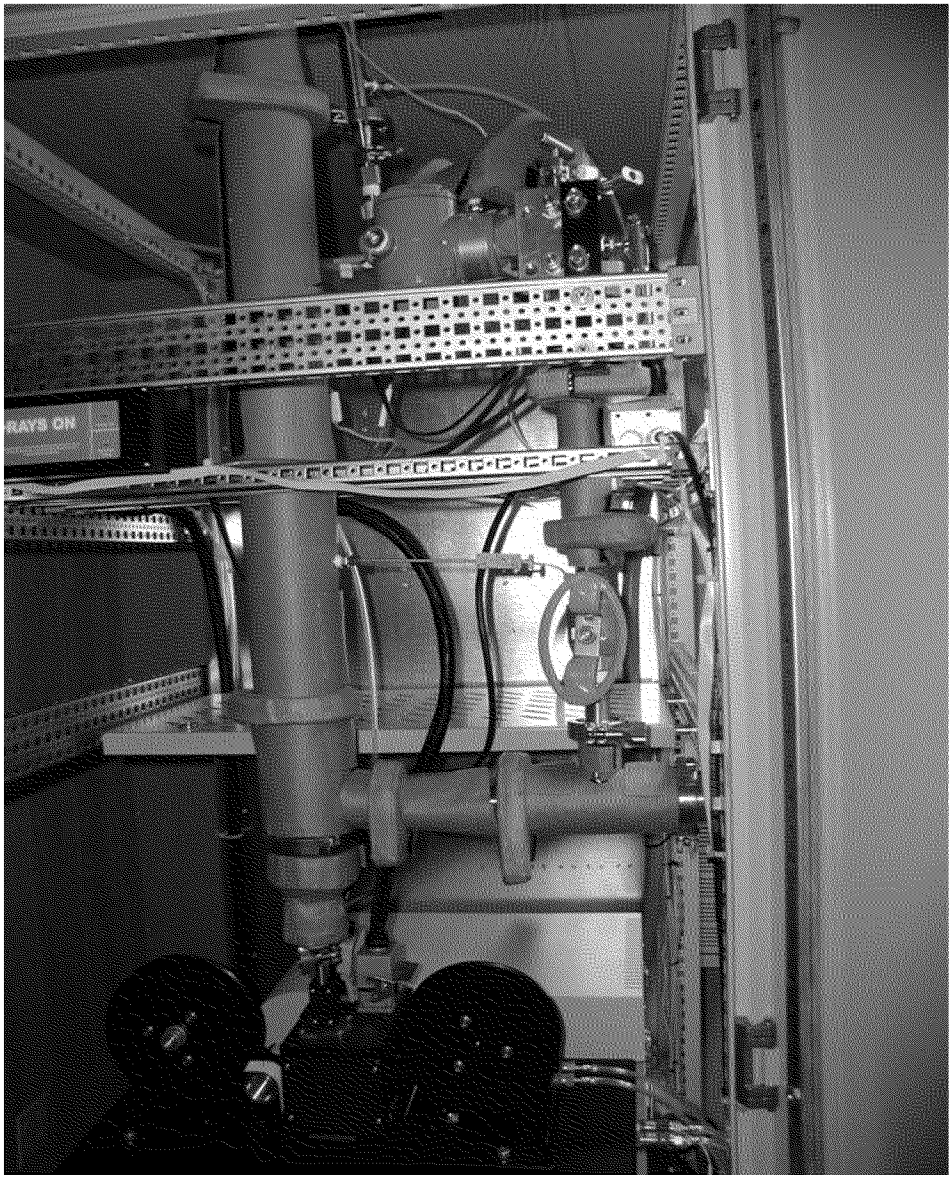

Figure 1. XCEM stilling chamber (vertical pipe) and sampling cassette (bottom).

Sampling and Analysis System

Approximately 0.8 liters per minute (Lpm) is extracted and concentrated on a filter tape for analysis. Following filtration, the extracted stack gas is transported to the XCEM chassis where drying and volume determination take place (Figure 2).

The sampling cassette holds a 4-week supply of filter tape on a reel-to-reel system that is automated to accurately move the tape from the sampling to an analysis position. Sampling and analysis occur simultaneously, resulting in a continuous monitoring system that reports metal concentration measurements every 10 to 20 minutes.

R5-2014-0104710000365

Figure 2. XCEM chassis.

Metal mass on the filter is determined using a modified ThermoNoran QuanX energy dispersive XRF analyzer. The QuanX is capable of simultaneously measuring 19 elements and a palladium (Pd) quality assurance (QA) standard. Although the QuanX can readily quantify elements with atomic number 13 and above, the XCEM-modified QuanX is most efficient at quantifying and reporting hazardous elements with an atomic number greater than 24 (Cr). Since XRF is nondestructive, the retentate on the filter tape can be reanalyzed if the end-user requires additional data.

Control System

The XCEM is controlled by a personal computer using a custom WonderWare® (Progressive Software Solutions, Inc., Albany, OR) software interface (Figure 3). All day-to-day functions of the XCEM are automated, including flow and temperature control, concentration determination, and QA routines. Flow, temperature, concentration, pressure, and error messages are automatically recorded in a secure database. The data can readily be imported into Excel or an equivalent program for subsequent evaluation. Flow, temperature, concentration, and pressure measurements are logged in real-time on the screen.

Execution of Field-Testing Activities

Before shipment to Tooele, the XCEM was tested and an initial calibration was completed. Due to a tight timetable for this project, a final calibration was not conducted until after the tests. Test data were modified according to the final calibration, resulting in an 8 percent increase in reported metal concentrations. All calibration adjustments were completed prior to receiving M29 results.

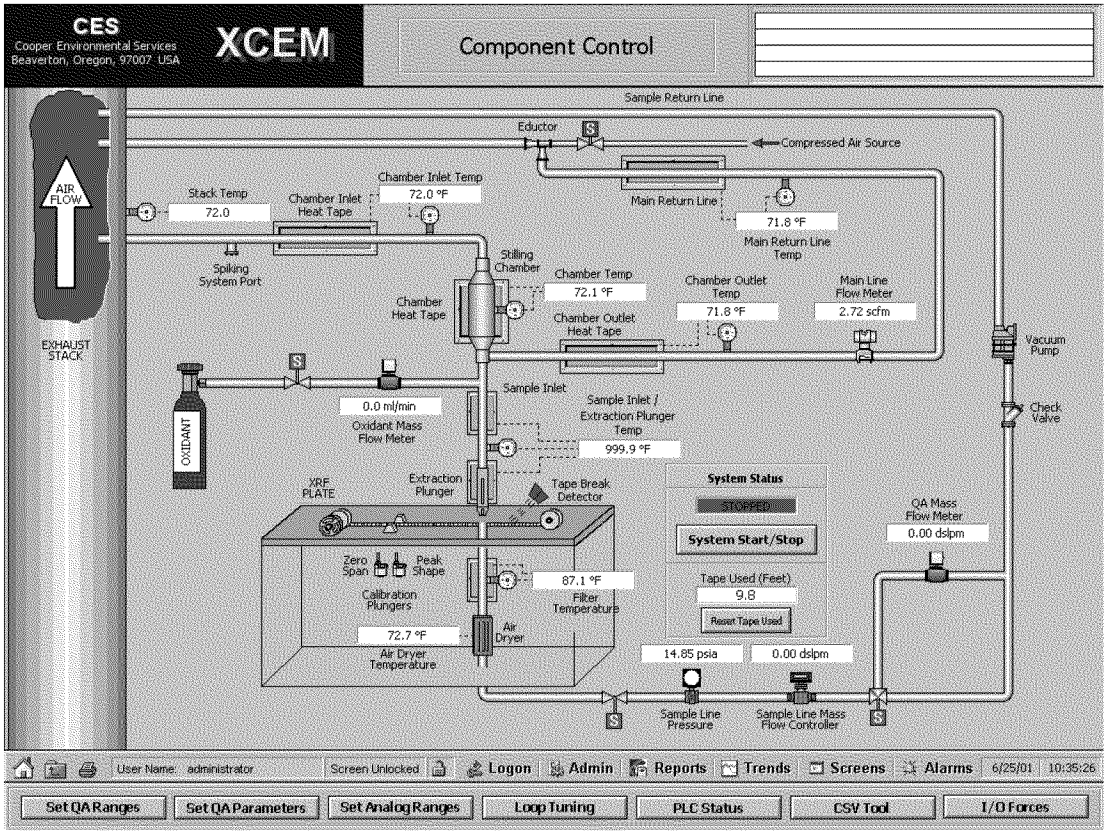

Figure 3. New Component Control Screen for XCEM software interface.

Following installation, preliminary onsite training was conducted for TEAD personnel. Onsite training consisted of an introduction to the XCEM and its capabilities. Although the XCEM has been designed for ease of use, it is recommended that additional training be provided to ensure successful integration of the XCEM into incinerator daily operations.

Test Plan

A test plan was developed to verify capabilities of the XCEM to measure metals under typical incinerator conditions (Appendix A). The test plan outlined methodology for comparison testing between EPA M29 and the XCEM at the TEAD incinerator. Specifically, the test plan called for at least 12 EPA M29 tests with each test run lasting 2 hours. Arsenic (As), barium (Ba), Cr, cadmium (Cd), nickel (Ni), mercury (Hg), antimony (Sb), and zinc (Zn) were spiked during the reference method testing to ensure quantifiable concentrations of a wide variety of metals. Lead was also measured for each test but was not spiked because it is found in quantifiable concentrations in TEAD incinerator emissions under normal operating conditions. The actual dates of the test, associated M29 run numbers, and TEAD incineration feedstream are shown in Table 3.

R5-2014-0104710000365

In general, the test plan (Appendix A) was followed as written with the following exceptions:

- The Army chose to burn bullets during the first two M29 tests rather than fuses as specified in the test plan.
- The XCEM observed high levels of Pb during the first two test runs. The TEAD operators believe that the high Pb was related to a faulty bypass valve. Consequently, the TEAD site manager decided to run M29 testing with no ammunition being incinerated until repairs could be completed. The repairs were completed after run 11.
- A 13th M29 test run was added.
- Delays in completing a trial burn test at the Army incinerator forced a 2-day postponement in XCEM testing. To make up for lost time, four M29 test runs were completed on both 15 and 16 May.

Table 3. XCEM test dates and associated TEAD incineration feedstream.

14 May			15 May				16 May				17 May	
Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11	Run 12	Run 13
50 Caliber	50 Caliber	No Ammo	No Ammo	No Ammo	No Ammo	No Ammo	No Ammo	No Ammo	No Ammo	No Ammo	MK344 Fuses	MK344 Fuses

EPA Verification

Test activities were coordinated with EPA's Environmental Technology Verification (ETV) program. ETV's charter is to provide objective and quality assured performance data on environmental technologies, so that users, developers, regulators, and consultants have an independent and credible assessment of an instrument's performance. Battelle Memorial Institute, headquartered in Columbus, OH, is EPA's partner for the ETV Advanced Monitoring Systems (AMS) Center. The scope of the AMS Center covers verification of monitoring methods for contaminants and natural species in air, water, and soil. For these tests, ETV representatives reviewed the test plan and monitored testing procedures. They also conducted an onsite audit of the Army laboratory that analyzed the M29 samples. CES provided ETV representatives with the XCEM metal concentrations for each test run. The M29 test results were submitted independently to the ETV representatives. These data, combined with an evaluation of the quality of the test, have been documented in a final ETV report (Myers et al. 2002).

TEAD Interface

The XCEM sampled the stack gas through a probe and transport line. Ideally, the probe would have been shrouded, which allows for increased flexibility in isokinetic sampling and reduces particulate loss in the probe. However, the shrouded probes are specially manufactured by Anderson Instruments, Inc.

R5-2014-0104710000365

(Smyrna, GA), and procuring the special probe requires significant lead time. With the short project timeline, a more easily built custom probe with a simpler design was supplied by Millennium Instruments, Inc (Spring Grove, IL). The probe was located at the same elevation as the reference method probes within 86 inches of the top of the stack. The XCEM and M29 probes were located approximately 27 feet above the base of the exhaust stack. The nearest flow disturbances were 9.8 duct diameters upstream (induced draft fan) and 4.3 duct diameters downstream (top of the stack) from the sample ports. These distances are adequate to ensure that these flow disturbances do not affect the sampling. The transport line consisted of approximately 35 ft of 1.5-in. diameter stainless steel tubing that extended from the probe to the XCEM shed, which was on the ground near the stack (Figure 4).

Test Objectives

The overall objective of the test was to provide quantitative verification of the performance of the XCEM under field conditions. EPA's draft performance specification document PS-10 (EPA 1996) is a proposed description of how to assess the acceptability of a multi-metal CEM upon installation and thereafter.

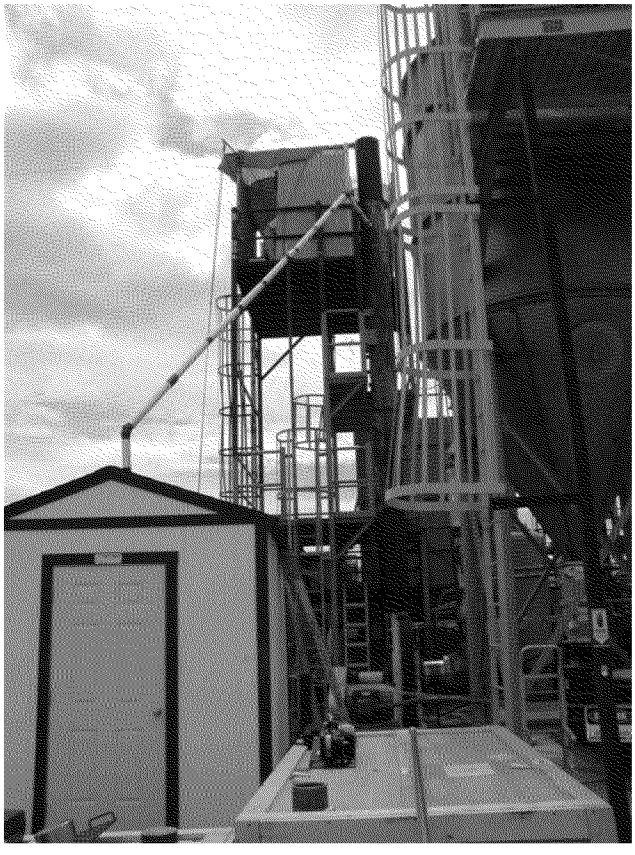

Figure 4. XCEM housing and transport line, M29 sampling setup, stack, and ceramic baghouse at TEAD.

R5-2014-0104710000365

The goals of the verification test were to meet the proposed PS-10 requirements for:

1. *Response time* and *reporting time* for a batch CEM.
2. *QA* by passing daily zero and calibration drift checks.
3. *Relative accuracy* for the elements in the feedstream of the TEAD incinerator (Sb, Ba, Cd, Cr, and Pb). This includes evaluating the response to change in concentration by testing at least one element at two concentration levels.

A secondary objective was to meet the RA criteria for additional regulated and unregulated metals, which are not typically found in the feedstream (As, Hg, Ni, and Zn).

Additional performance parameters examined during the testing included:

- correlation with reference method
- precision
- low-level metal response
- bias.

The XCEM has an automated check for calibration drift that measures a Pd standard with each XCEM test run. Calibration drift was also checked by the automated daily XCEM zero and upscale QA measurements. For the verification test, response time was determined as the time between the start of one sampling period and the beginning of a second sampling period. The effectiveness of the XCEM to measure low concentrations was determined by a comparison to Cr and As reference method concentrations. Bias was identified using EPA Method 301 – Field Validation of Pollutant Measurement Methods from Various Waste Media (EPA 1992).

It was beyond the scope of this verification test to durability for routine long-term use. This test evaluated the performance of a new XCEM over a relatively short test period, operated by skilled personnel. It must be noted that the long-term performance may be different from that observed in the testing described here. The XCEM did not exhibit any mechanical problems during the test; it completed more than 150 test runs during the week without any downtime.

Site Description

Verification testing took place at TEAD building 1320 deactivation incinerator APE-1236. The TEAD incinerator, which runs on diesel fuel, is designed to incinerate decommissioned munitions. Typical operating parameters for the incinerator are shown in Table 4. The TEAD incinerator is classified as a dry stack

with water content ranging from 5 to 10 percent. Typical stack PM concentrations are in the range of 10 micrograms per dry standard cubic meter.

The TEAD incinerator is currently regulated under the Resource Conservation and Recovery Act (RCRA) for Sb, As, Ba, beryllium (Be), Cd, Cr, Pb, Hg, Ni, selenium (Se), silver (Ag), and thallium (Tl). Of the 12 regulated elements, 5 are typically found in the feedstream: Sb, Ba, Cd, Cr, and Pb. The XCEM was tested for its measurement capabilities of the five elements found in the feedstream as well as As, Hg, Ni, and a nonregulated metal, Zn. These elements were selected in order to challenge the XCEM over a large range of analysis conditions and elemental concentrations.

For the verification test, metals in the TEAD incinerator stack gas were regulated under a Temporary Authorization permit (Table 5). Of the 12 regulated metals, Pb is the only element that was consistently found in measurable concentrations in the stack gas. Figure 5 shows the deactivation incinerator set up and the locations for sampling and spiking during the test.

Table 4. Typical operating parameters for the APE-1236 deactivation furnace.

Temp. (°F)	1630
Baghouse ΔP (in. H_2O)	4
Baghouse Inlet Temperature (°F)	860
Kiln Feed End Draft Pressure (in. H_2O)	-0.2
Kiln Feed End Temperature (°F)	375
Kiln Burner End Temperature (°F)	1000
O_2 – CEM (%)	15
CO (ppm)	8
Stack Temperature (°F)	500
Stack Gas Velocity (ft/sec)	46

Table 5. TEAD metal emission limits during verification testing.

Element	Limit (g/hr)	Element	Limit (g/hr)
Antimony	14	Lead	4.3
Arsenic	0.11	Mercury	14
Barium	2400	Nickel	930
Beryllium	0.20	Selenium	180
Cadmium	0.26	Silver	140
Chromium	0.04	Thallium	14

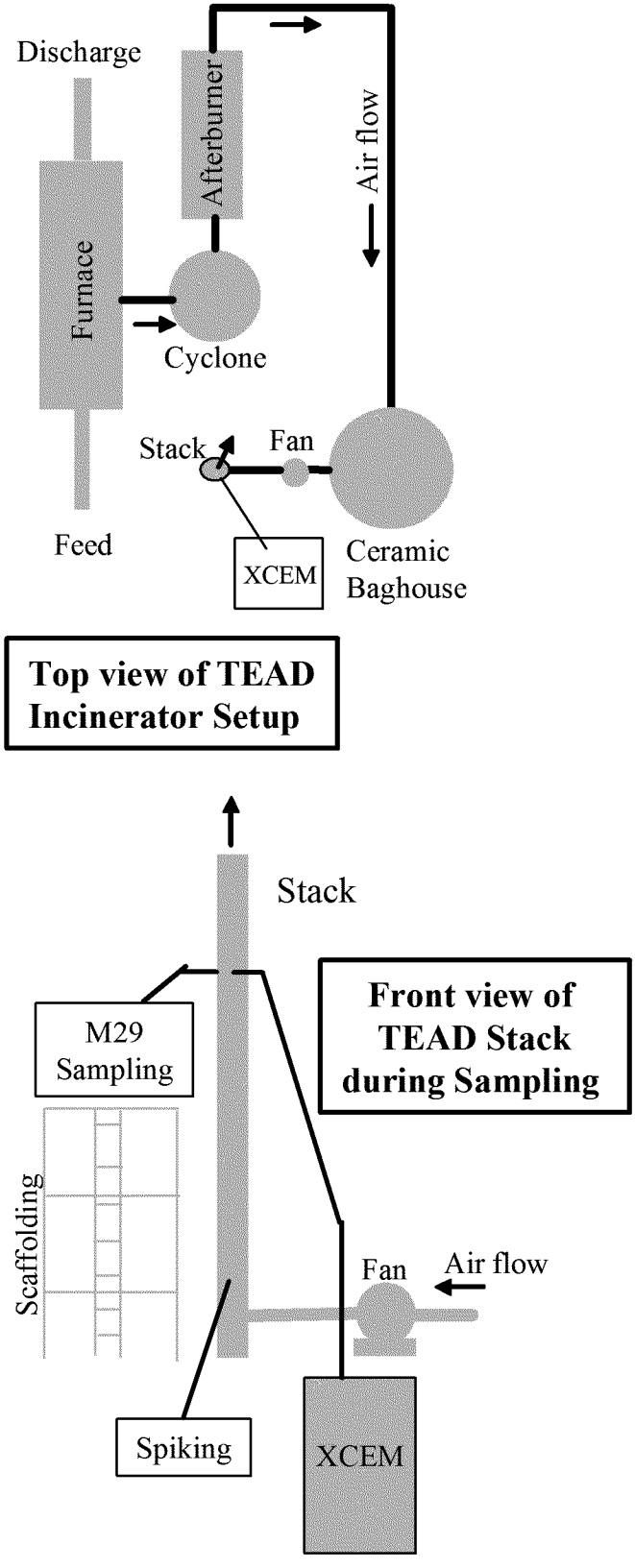

Figure 5. TEAD incinerator setup and sampling/spiking locations.

Experimental Design

Both the kiln and afterburner were fired with diesel fuel for all 13 runs. During runs 1 and 2, 50-caliber bullets were incinerated. The XCEM observed unexpected high Pb concentrations during these runs, however, which led to a decision not to incinerate additional ammunition during the test until repairs to a bypass valve could be made. For this reason, no ammunition was burned during runs 3 through 11. Following the bypass repair, two final M29 runs were conducted while incinerating Mark 344 fuses. Table 6 shows the 9 elements that were measured by the XCEM during all 13 of the verification test runs. Eight of these metals were spiked directly into the stack downstream of the controls. These metals were spiked at the level shown in Table 6. Lead, however, was not spiked since the incinerated munitions provide measurable concentrations of Pb without spiking.

Spiking was conducted by MSE-TA using three atomizers to inject solutions containing the metals directly into the stack (Figure 6). Manufacturer specifications for the atomizers determine droplet size distributions based on pressure and airflow rate. For these tests, pressure and flow rate were maintained to keep droplet sizes less than 28 microns in diameter. When dried, the majority of the particle mass was calculated to be in the 1 to 4 micron diameter range. An analysis of the M29 concentration data during validation testing indicated that 10 to 15 percent of the spiked metal mass was lost on the probe (CHPPM 2001). This level of probe loss is typical for M29 at an incinerator and, since particulate loss in the probe depends in part on particle size, indicates that the spiked metal particle size was on the same order as a typical incinerator.

Table 6. TEAD incinerator metal emission limits and spiking levels.

Elements	Emission Limits[1]		Spiking Level[1]	
	g/hr	~ µg/dscm	~ µg/dscm	
			Runs 1-6	Runs 7-13
As	0.11	25	14	14
Ba	2,400	540,000	200	200
Cd	0.26	58	34	34
Cr	0.04	10	5	5
Hg	14	3,145	280	88
Ni	930	209,000	460	180
Pb	4.3	966	NS	NS
Sb	14	3145	520	200
Zn	NR	NR	460	180

[1] The concentration in µg/dscm assumes a stack flow rate of about 4500 dscm/hr

NR: Not regulated NS: Not spiked

R5-2014-0104710000365

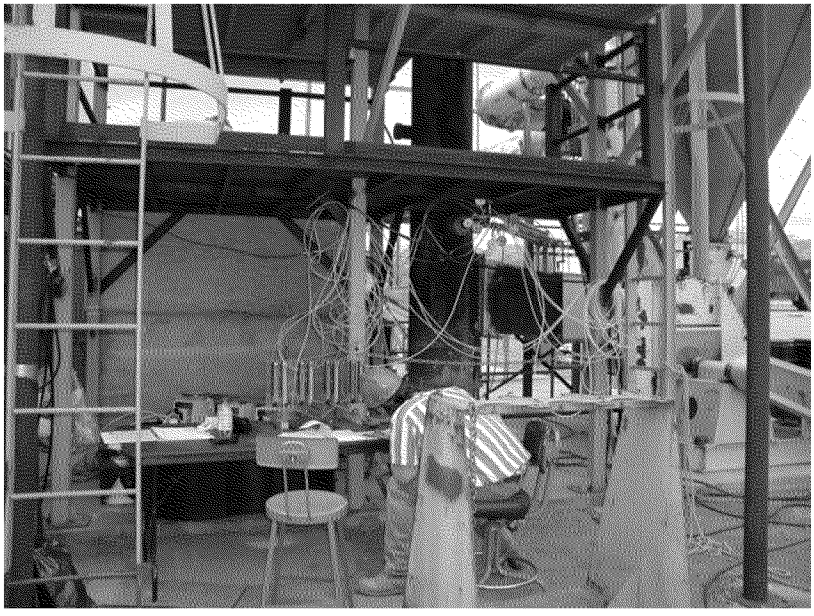

Figure 6. Spiking at base of stack during validation testing.

Three separate solutions were prepared for spike injection. The first solution contained arsenic oxide (As_2O_5), Cd metal, and chromium oxide (CrO_3) dissolved in a dilute nitric acid solution. The second solution contained mercury nitrate ($Hg(NO_3)_2$), nickel nitrate ($Ni(NO_3)_2$), and zinc oxide (ZnO) dissolved in a dilute nitric acid. The final solution contained antimony tartrate ($K_2(C_4H_2O_6Sb)_2$) and barium nitrate ($Ba(NO_3)_2$) dissolved in water (Bryson 2001).

A total of 13 dual M29 test runs were performed over a 4-day period (14–17 May) by the U.S. Army CHPPM Air Quality Surveillance Program. The M29 trains sampled for 2 hr while XCEM data were recorded every 20 minutes and were averaged for comparison to each M29 test run. As a performance audit, two blank trains were quantitatively spiked with all nine of the metals.

CHPPM's Directorate of Laboratory Services (DLS) conducted laboratory analysis of the sampling trains.

Results

XCEM Reported Concentrations

Time-weighted average concentrations

Average XCEM concentrations during the time of one M29 test run were calculated using Equation 1.

$$C_i = \frac{\sum_{j=1}^{n} C_{ij} t_j}{\sum t_j} \qquad \textbf{[Eq 1]}$$

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.

Data corrections

Following M29 testing, but prior to receiving M29 results, CES recalibrated the XCEM and determined that a 4.4 percent global change was required for XCEM reported concentrations. In addition to the recalibration, CES conducted extensive testing of the sample line dryer and determined that a 3.5 percent correction in flow was required since the dryer did not remove all of the moisture in the line. The net result of these changes was to uniformly increase the reported XCEM concentrations by about 8 percent. Appendix B includes a complete discussion of these changes.

In addition to the global changes, it was determined that a spectral interference between Pb and As was affecting As concentrations. For this reason, As concentrations were corrected for the Pb interference as discussed in **Response to Changes in Metal Concentration** (page 25). Arsenic corrections were completed prior to receiving M29 data.

The final reported XCEM concentrations are listed in Table 7. Approximately six to seven XCEM measurement took place during each M29 run. The "Min. of Run" column in Table 7 refers to the number of minutes for that particular XCEM (listed as XC in the table) measurement that coincided with the M29 run.

R5-2014-0104710000365

Table 7. Final reported CEM concentrations (µg/dscm) for M29 testing.

RM No.	Date	Start	Stop	XC No.	Min. of Run	XC Time	As	Ba	Cd	Cr	Hg	Ni	Pb	Sb	Zn	Pd
Run 1	5/14/01	10:45	11:05	650	5.0	19:48.0	20.8	166	27.7	3.1	59	343	1,102	340	297	24.1
Run 1	5/14/01	11:05	11:26	651	21.2	21:12.0	24.3	171	26.0	2.5	109	436	1,127	372	316	23.8
Run 1	5/14/01	11:26	11:48	652	21.5	21:32.0	21.1	192	26.5	1.9	156	467	1,149	361	320	25.6
Run 1	5/14/01	11:48	12:09	653	21.7	21:42.0	20.7	165	21.8	2.2	207	449	1,196	353	316	25.5
Run 1	5/14/01	12:10	12:31	654	21.7	21:41.0	25.3	187	28.2	2.6	242	470	1,319	377	342	24.6
Run 1	5/14/01	12:31	12:53	655	21.9	21:51.0	21.5	218	31.8	2.2	257	515	1,607	399	372	25.4
Run 1	5/14/01	12:53	13:15	656	7.0	22:07.0	23.8	202	27.2	2.4	283	463	709	386	348	24.2
Time Weighted Avg.					**120.0**	**21:24.7**	**22.6**	**187**	**26.9**	**2.3**	**194**	**462**	**1,240**	**372**	**333**	
Run 2	5/14/01	13:58	14:23	659	18.3	25:09.0	7.3	230	26.8	2.3	186	375	3,422	360	299	25.6
Run 2	5/14/01	14:23	14:46	660	22.9	22:56.0	3.5	224	29.5	2.0	234	427	3,248	379	345	24.7
Run 2	5/14/01	14:46	15:09	661	22.9	22:56.0	13.0	249	26.0	1.2	244	427	3,017	398	352	25.1
Run 2	5/14/01	15:09	15:32	662	22.9	22:54.0	23.8	250	22.3	2.0	220	405	2,683	370	332	25.3
Run 2	5/14/01	15:32	15:55	663	22.6	22:36.0	31.5	194	29.1	1.2	239	415	2,347	379	347	25.2
Run 2	5/14/01	15:55	16:17	664	10.3	22:34.0	17.8	172	27.1	2.6	257	392	182	348	319	24.4
Time Weighted Avg.					**120.0**	**23:10.8**	**16.3**	**224**	**26.8**	**1.8**	**229**	**410**	**2,690**	**375**	**335**	
Run 3	5/14/01	17:00	17:23	667	16.0	22:45.0	15.3	127	25.4	3.4	259	395	118	334	320	24.6
Run 3	5/14/01	17:23	17:44	668	21.0	21:00.0	13.1	140	21.3	2.2	264	388	91	335	319	25.2
Run 3	5/14/01	17:44	18:05	669	20.9	20:52.0	13.0	158	27.0	2.5	265	417	60	355	341	25.4
Run 3	5/14/01	18:05	18:26	670	21.0	20:58.0	13.1	175	28.9	2.9	268	409	55	363	339	25.7
Run 3	5/14/01	18:26	18:47	671	20.9	20:53.0	14.2	168	21.4	2.4	255	413	60	352	333	24.6
Run 3	5/14/01	18:47	19:07	672	20.3	20:54.0	11.2	147	24.0	2.3	249	414	65	360	347	25.9
Time Weighted Avg.					**120.0**	**21:13.7**	**13.2**	**154**	**24.6**	**2.6**	**260**	**406**	**73**	**351**	**334**	
Run 4	5/15/01	8:59	9:18	684	3.3	19:43.0	13.2	145	21.5	4.5	33	294	69	271	235	25.0
Run 4	5/15/01	9:18	9:39	685	20.6	20:34.0	15.0	173	28.5	6.2	54	401	69	333	319	23.4
Run 4	5/15/01	9:39	10:00	686	20.9	20:55.0	15.6	133	33.2	5.4	69	432	66	362	349	24.7
Run 4	5/15/01	10:00	10:21	687	21.0	21:00.0	16.2	154	30.5	5.3	80	432	64	371	348	23.7
Run 4	5/15/01	10:21	10:42	688	21.0	20:58.0	16.6	191	32.1	5.0	84	433	64	378	344	25.1
Run 4	5/15/01	10:42	11:03	689	21.0	20:57.0	15.2	145	26.6	5.2	85	418	55	361	339	24.2
Run 4	5/15/01	11:03	11:24	690	12.3	20:51.0	17.4	183	28.5	5.5	98	446	45	380	366	25.0
Time Weighted Avg.					**120.0**	**20:42.6**	**15.8**	**161**	**29.8**	**5.4**	**76**	**422**	**62**	**361**	**340**	
Run 5	5/15/01	12:06	12:27	693	15.6	20:55.0	18.0	177	31.4	5.5	93	440	49	383	355	24.7
Run 5	5/15/01	12:27	12:48	694	20.9	20:52.0	16.2	172	33.7	5.5	97	430	54	371	348	24.3
Run 5	5/15/01	12:48	13:09	695	20.9	20:51.0	16.0	153	34.4	6.1	102	417	52	362	339	23.3
Run 5	5/15/01	13:09	13:30	696	20.8	20:48.0	17.3	182	33.4	5.3	114	450	47	386	360	24.6
Run 5	5/15/01	13:30	13:51	697	21.0	20:57.0	14.3	185	35.8	5.7	122	449	45	393	365	25.7
Run 5	5/15/01	13:51	14:12	698	21.0	20:59.0	17.0	181	32.2	5.4	129	443	38	390	358	25.2
Time Weighted Avg.					**120.0**	**20:53.7**	**16.4**	**175**	**33.6**	**5.6**	**110**	**438**	**47**	**381**	**354**	
Run 6	5/15/01	14:54	15:15	701	7.2	20:57.0	17.8	166	31.4	5.4	137	455	39	392	376	25.6
Run 6	5/15/01	15:15	15:36	702	21.0	20:59.0	15.5	152	31.9	5.4	146	465	39	386	379	24.9
Run 6	5/15/01	15:36	15:57	703	21.0	20:58.0	12.4	167	31.4	5.4	142	443	48	387	362	24.4
Run 6	5/15/01	15:57	16:18	704	20.9	20:56.0	12.9	165	31.3	5.9	140	430	47	372	350	26.2
Run 6	5/15/01	16:18	16:39	705	20.9	20:54.0	14.0	187	34.1	5.3	168	427	36	381	353	24.9
Run 6	5/15/01	16:39	17:00	706	20.9	20:55.0	15.2	185	32.9	5.5	164	442	35	389	363	24.5
Run 6	5/15/01	17:00	17:21	707	8.2	20:58.0	13.7	164	36.7	6.2	166	462	46	387	369	25.0
Time Weighted Avg.					**120.0**	**20:56.7**	**14.2**	**170**	**32.6**	**5.6**	**152**	**443**	**41**	**384**	**363**	
Run 7	5/15/01	18:03	18:24	710	18.1	20:55.0	16.9	183	35.6	5.8	154	477	45	396	386	24.9
Run 7	5/15/01	18:24	18:45	711	21.0	20:58.0	18.5	166	34.5	6.4	134	478	44	404	395	24.2
Run 7	5/15/01	18:45	19:06	712	21.0	20:58.0	16.5	191	28.8	6.0	120	491	45	377	377	25.3
Run 7	5/15/01	19:06	19:27	713	21.0	20:59.0	16.1	168	30.9	5.6	121	459	40	375	359	25.3
Run 7	5/15/01	19:27	19:48	714	20.8	20:50.0	16.2	175	30.7	5.7	132	419	34	367	337	25.9
Run 7	5/15/01	19:48	20:09	715	18.1	20:41.0	15.1	159	33.3	5.5	137	436	30	379	351	24.3
Time Weighted Avg.					**120.0**	**20:53.5**	**16.6**	**174**	**32.2**	**5.8**	**132**	**461**	**40**	**383**	**367**	

Table 7 (Cont'd). Final reported XCEM concentrations (μg/dscm) for M29 testing.

RM No.	Date	Start	Stop	XC No.	Min. of Run	XC Time	As	Ba	Cd	Cr	Hg	Ni	Pb	Sb	Zn	Pd
Run 8	5/16/01	8:58	9:18	725	15.3	20:24.0	17.6	111	32.5	5.2	17	193	290	141	134	23.8
Run 8	5/16/01	9:18	9:39	726	20.6	20:33.0	20.3	139	31.8	6.0	20	220	242	134	150	24.2
Run 8	5/16/01	9:39	10:00	727	20.6	20:33.0	16.5	145	32.3	5.4	22	222	231	125	151	25.6
Run 8	5/16/01	10:00	10:20	728	20.6	20:33.0	18.0	156	29.4	5.3	28	197	199	136	148	24.6
Run 8	5/16/01	10:20	10:41	729	20.4	20:26.0	12.5	176	36.3	5.1	33	204	202	135	141	24.4
Run 8	5/16/01	10:41	11:01	730	20.4	20:24.0	18.7	152	32.7	5.7	36	216	226	134	150	24.3
Run 8	5/16/01	11:01	11:22	731	2.3	20:30.0	17.1	162	32.4	5.7	44	226	214	141	150	23.9
Time Weighted Avg.					**120.0**	**20:29.0**	**17.3**	**148**	**32.5**	**5.4**	**27**	**210**	**229**	**134**	**146**	
Run 9	5/16/01	11:42	12:03	733	7.1	20:28.0	21.1	183	33.1	4.5	49	210	190	136	147	25.0
Run 9	5/16/01	12:03	12:23	734	20.4	20:26.0	14.8	170	32.7	5.6	50	201	170	139	142	24.0
Run 9	5/16/01	12:23	12:44	735	20.4	20:21.0	18.8	154	30.7	5.3	49	204	162	142	146	24.1
Run 9	5/16/01	12:44	13:04	736	20.3	20:18.0	16.6	206	35.4	6.5	56	223	191	154	152	24.9
Run 9	5/16/01	13:04	13:25	737	20.4	20:24.0	17.0	143	31.1	5.2	54	215	151	145	145	24.7
Run 9	5/16/01	13:25	13:45	738	20.3	20:19.0	18.6	138	28.8	5.2	59	200	153	145	144	24.5
Run 9	5/16/01	13:45	14:05	739	11.1	20:23.0	16.0	151	29.1	5.2	60	228	155	148	143	25.1
Time Weighted Avg.					**120.0**	**20:22.7**	**17.3**	**162**	**31.6**	**5.5**	**54**	**210**	**166**	**145**	**146**	
Run 10	5/16/01	14:46	15:07	742	17.2	20:24.0	19.2	156	34.7	6.0	91	210	146	148	146	25.2
Run 10	5/16/01	15:07	15:27	743	20.4	20:21.0	22.3	187	37.0	5.4	89	216	261	154	151	25.6
Run 10	5/16/01	15:27	15:48	744	20.4	20:23.0	17.0	141	32.5	5.4	82	192	115	134	133	24.9
Run 10	5/16/01	15:48	16:08	745	20.3	20:16.0	17.1	192	31.6	5.4	91	208	134	146	149	25.6
Run 10	5/16/01	16:08	16:28	746	20.4	20:21.0	17.5	161	36.2	5.5	95	208	108	163	145	24.2
Run 10	5/16/01	16:29	16:49	747	20.3	20:20.0	18.3	167	30.9	5.6	95	203	95	140	137	24.7
Run 10	5/16/01	16:49	17:09	748	1.2	20:20.0	12.7	139	29.9	5.4	109	186	110	152	137	24.5
Time Weighted Avg.					**120.0**	**20:20.7**	**18.5**	**167**	**33.8**	**5.5**	**91**	**206**	**143**	**147**	**143**	
Run 11	5/16/01	17:32	17:52	750	6.3	20:21.0	15.7	178	31.3	6.0	101	211	108	150	143	25.0
Run 11	5/16/01	17:52	18:12	751	20.3	20:18.0	15.8	147	30.2	5.2	96	209	102	147	141	25.5
Run 11	5/16/01	18:12	18:33	752	20.3	20:20.0	15.5	170	29.3	5.3	95	204	104	141	145	24.6
Run 11	5/16/01	18:33	18:53	753	20.3	20:18.0	16.4	178	30.2	5.4	95	192	91	147	138	25.6
Run 11	5/16/01	18:53	19:13	754	20.2	20:12.0	17.3	152	26.4	5.8	96	191	89	147	141	24.8
Run 11	5/16/01	19:13	19:34	755	20.2	20:12.0	17.2	167	32.8	5.5	92	201	89	143	146	24.9
Run 11	5/16/01	19:34	19:54	756	12.3	20:17.0	15.0	152	33.2	4.6	84	212	96	147	145	24.0
Time Weighted Avg.					**120.0**	**20:16.9**	**16.2**	**163**	**30.2**	**5.4**	**94**	**201**	**96**	**145**	**143**	
Run 12	5/17/01	11:12	11:32	770	13.0	20:01.0	17.8	174	26.5	4.1	24	224	170	137	133	24.6
Run 12	5/17/01	11:32	11:52	771	20.1	20:08.0	17.2	195	23.2	4.2	35	238	232	159	146	25.9
Run 12	5/17/01	11:52	12:12	772	20.2	20:14.0	20.5	174	30.5	4.3	55	222	273	165	157	25.3
Run 12	5/17/01	12:12	12:32	773	20.3	20:16.0	16.7	226	24.4	4.0	73	221	204	158	161	25.4
Run 12	5/17/01	12:32	12:53	774	20.2	20:12.0	18.4	153	31.7	4.8	79	206	161	158	151	24.1
Run 12	5/17/01	12:53	13:13	775	20.2	20:12.0	12.3	177	28.0	4.5	83	204	138	155	143	24.4
Run 12	5/17/01	13:13	13:33	776	6.0	20:07.0	14.1	150	28.2	4.1	86	191	140	155	151	26.0
Time Weighted Avg.					**120.0**	**20:10.0**	**17.0**	**182**	**27.5**	**4.3**	**62**	**218**	**195**	**156**	**150**	
Run 13	5/17/01	14:14	14:34	779	6.1	20:15.0	19.1	162	35.9	5.1	80	201	119	171	146	24.0
Run 13	5/17/01	14:34	14:54	780	20.2	20:10.0	19.9	210	33.9	5.3	80	213	122	170	146	25.3
Run 13	5/17/01	14:54	15:14	781	20.2	20:09.0	17.4	159	36.1	6.1	82	235	117	168	149	25.0
Run 13	5/17/01	15:14	15:34	782	20.2	20:10.0	20.3	140	33.8	5.8	83	212	112	170	150	25.1
Run 13	5/17/01	15:35	15:55	783	20.2	20:12.0	21.3	196	40.7	5.9	84	173	129	169	117	24.4
Run 13	5/17/01	15:55	16:15	784	20.0	20:02.0	19.2	165	39.1	6.0	74	170	121	166	82	25.1
Run 13	5/17/01	16:15	16:35	785	13.1	19:57.0	8.3	94	18.7	4.0	46	70	85	77	22	25.2
Time Weighted Avg.					**120.0**	**20:07.9**	**18.4**	**165**	**34.7**	**5.6**	**77**	**186**	**116**	**159**	**118**	

Sampling and Response Time

The XCEM met PS-10 sampling and response time criteria for a batch CEM. These criteria are that (1) the sampling time be no longer than one-third of the averaging period for the applicable standard, (2) the delay between the end of the sampling period and reporting of the sample analysis shall be no greater than 1 hour, and (3) sampling is to be continuous except in that the pause in sampling when sample collection media are changed should be no greater than 5 percent for the averaging period or 5 minutes, whichever is less (EPA 1996). Exhibiting no mechanical problems, the XCEM had an effective up-time of 100 percent during the 40 hours of verification testing. The XCEM sampled continuously except for a 4-second period between each 20-minute sample run when the filter tape was moved to a new analysis position. XCEM results are reported immediately after each 20-minute analysis resulting in a 20-minute response time between the end of sampling and reporting.

Zero and Calibration Drift

The XCEM has automated daily zero and upscale checks and reports a Pd concentration with each sample to test for calibration drift. To determine the zero check, the XCEM measures an unexposed region of the filter tape. Following the zero check, a plunger is extended into the analysis region. The tip of the plunger contains Cr, Cd, Hg, and Pb embedded in a resin. Analysis of this spiked resin provides an upscale check for the XCEM.

Zero and upscale checks were conducted on each of the four test days with the results shown in Table 8. Since the zero and upscale checks are evaluations of mass measurements, they are reported as mass per unit area on the filter (µg/spot). Equivalent zero and upscale concentrations in micrograms per dry standard cubic meter are also shown in Table 8 and reflect the typical sampling rate of 16 L per spot.

Zero values determined during the TEAD test indicate no measurable blank bias in the mass measurement. The XCEM detection limits for Cr, Cd, Hg, and Pb are 0.75, 3.0, 1.0, and 1.0 µg/dscm, respectively. The XCEM zero values were below the detection limits for Cd, Hg, and Pb and only slightly higher than the Cr detection limit.

The upscale check indicated good precision for the high concentration mass measurements. The precision over the 4 days was less than 1 percent for Cd, Hg, and Pb and about 2.3 percent for the Cr.

Table 8. Upscale and zero concentrations during validation testing.

Date	Upscale Values (µg)				Zero Values (µg)[1]			
	Cr	Cd	Hg	Pb	Cr	Cd	Hg	Pb
5/14/01	5.23	156	27.6	30.4	0.012	0.046	0.008	0.008
5/15/01	5.53	158	28.0	30.9	0.016	0.042	0.008	0.008
5/16/01	5.45	156	27.9	30.8	0.014	0.024	0.010	0.008
5/17/01	5.42	156	27.9	30.6	0.011	0.024	0.005	0.023
Avg.	5.41	157	27.8	30.7	0.013	0.034	0.008	0.012
SD	0.13	0.74	0.18	0.23				
%RSD	2.33	0.47	0.65	0.76				
Date	Equiv. Upscale Values (µg/dscm)[2]				Equiv. Zero Values (µg/dscm)[1,2]			
	Cr	Cd	Hg	Pb	Cr	Cd	Hg	Pb
5/14/01	327	9,765	1,724	1,898	0.75	2.86	0.50	0.47
5/15/01	346	9,850	1,750	1,931	1.01	2.65	0.50	0.50
5/16/01	341	9,772	1,742	1,925	0.85	1.50	0.63	0.50
5/17/01	339	9,744	1,746	1,912	0.67	1.50	0.29	1.42
Avg.	338	9,783	1,741	1,917	0.82	2.13	0.48	0.72
SD	7.88	46.14	11.25	14.64				
%RSD	2.33	0.47	0.65	0.76				

1) Gray values were nondetects. Nondetect treated as one-half of Detection Limit.
2) Equivalent concentrations determined using 16 liters per sample.
SD = standard deviation; RSD = relative standard deviation

Palladium, which is measured with every sample, also displayed good precision over the 4 days of testing (Figure 7). Overall, the Pd concentration had a precision of about 2.5 percent with all 113 measured Pd concentrations lying within 6 percent of the average concentration. Analysis of the Pd concentration trend in Figure 7 indicates that no significant drift occurred. Over the 4-day test period, the average Pd concentration changed by less than 1 percent with no observable trending occurring.

Correlation with Reference Method

The comparison between the XCEM and M29 concentration measurements are shown in Figure 8. In this figure the dashes represent the M29 concentration over the sampling period, while the diamonds represent the individual XCEM measurements. The degree of correlation between the XCEM and M29 is shown in Figure 9 and Table 9. Five metals (Ni, Pb, Sb, Zn, and Hg) were present in the stack gas at varying concentrations. Of these elements, Ni, Sb, and Zn showed correlations of 0.95 or better. Lead shows a high correlation of 0.997 for all 13 runs, but a correlation of 0.76 for the 11 runs in which Pb concentrations were used for RA comparisons. Mercury did not show a high correlation between the two methods.

R5-2014-0104710000365

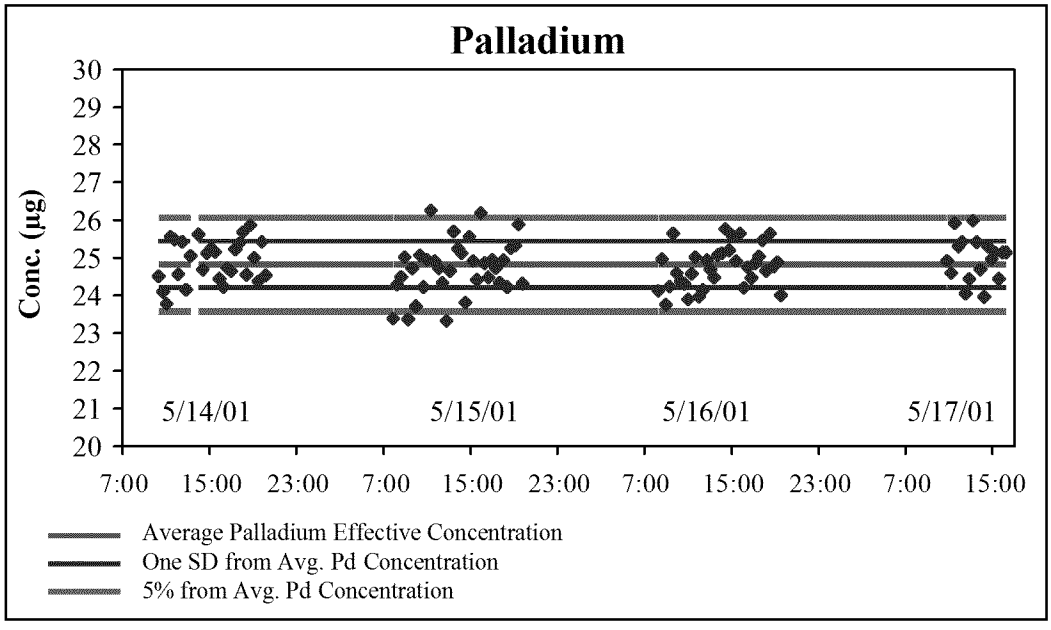

Figure 7. Palladium concentrations during M29 testing.

Unlike the other elements, the XCEM Hg concentrations were consistently lower than M29, but by a variable amount. During the early runs for each day, the XCEM reported low concentrations relative to M29. As the day progressed, the XCEM Hg concentration would gradually increase until it approximated M29 reported concentrations. This same increasing Hg concentration trend was observed on each of the four test days (Figure 8).

It is believed that the Hg was lost during transport from the stack to the XCEM. The M29 samples were collected next to the stack and were not transported through a long sample line as the XCEM samples were. The TEAD incinerator was shut down each evening and started in the morning 1 hour before validation testing. Consequently, the transport line, which was insulated but not heat-traced, was cooler during the early runs. Some research indicates that Hg can be lost to a stainless steel surface at low temperatures (Hall et al. 1990; Wang et al. 1983). In the laboratory, the XCEM was tested with oxidized Hg and met with good success (Hay et al. 2005). The laboratory tests, however, were conducted at elevated line temperatures. It is recommended that a shrouded probe and heat-traced tubing be used to overcome potential Hg transport problems.

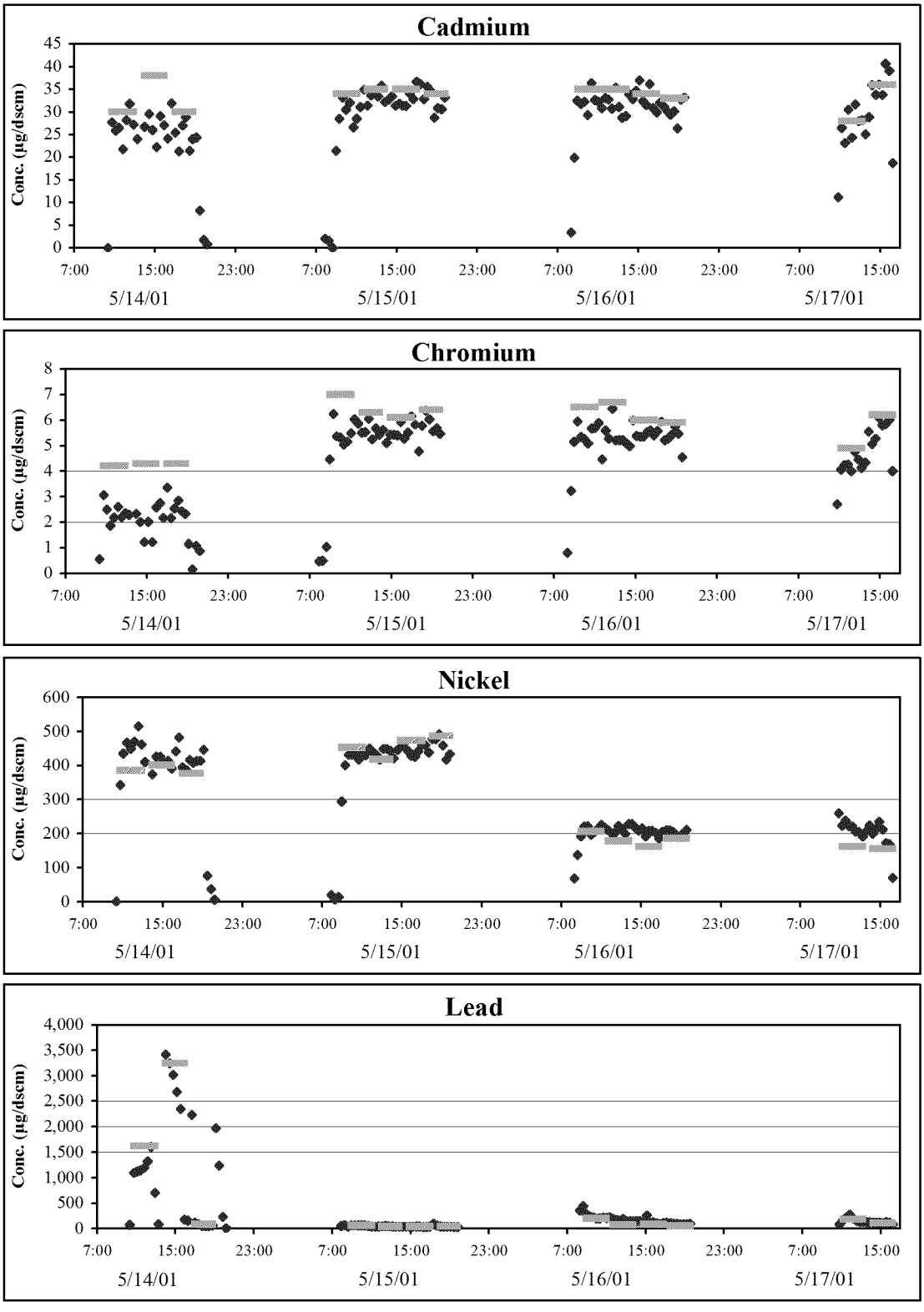

Figure 8. XCEM and M29 concentrations during TEAD verification testing.

R5-2014-0104710000365

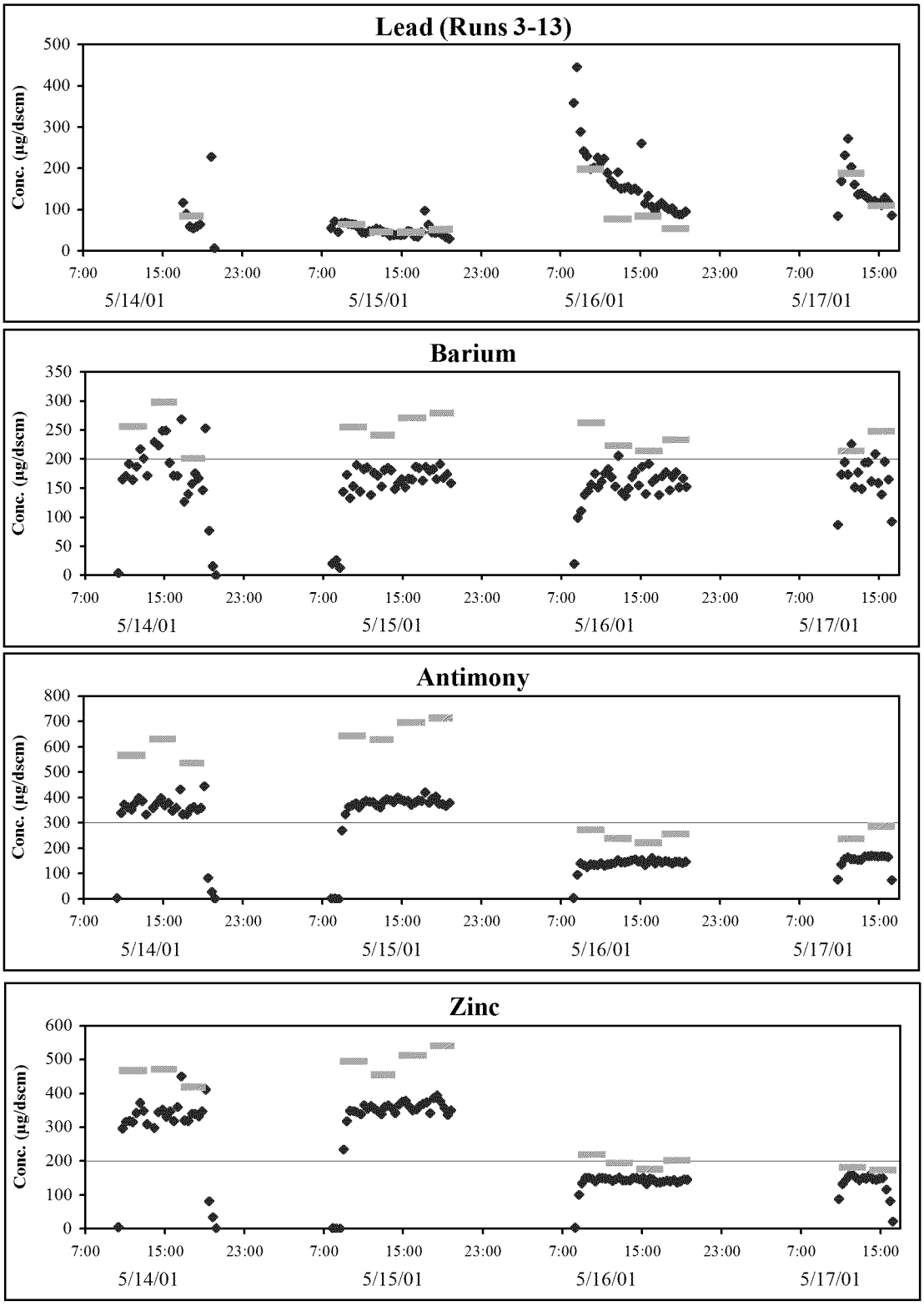

Figure 8 (Cont'd). XCEM and M29 concentrations during TEAD verification testing.

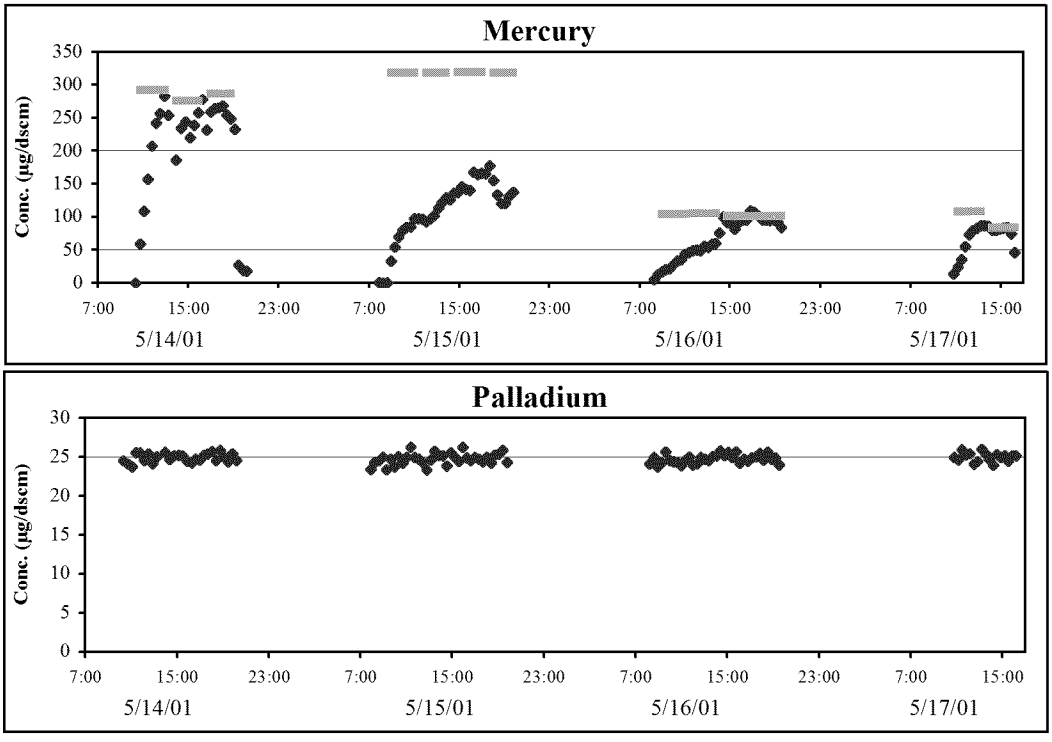

Figure 8 (Cont'd). XCEM and M29 concentrations during TEAD verification testing.

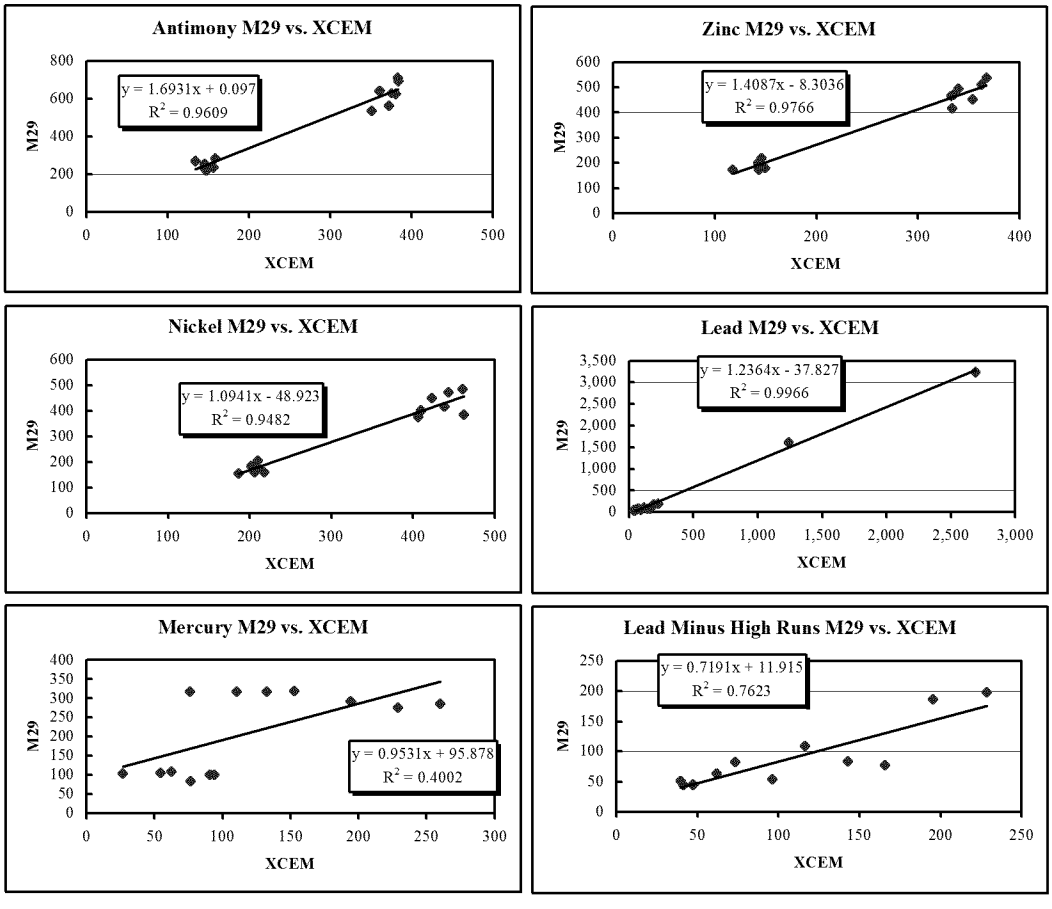

Figure 9. Correlation between XCEM and M29 for elements spiked at two levels.

Table 9. Correlation between the XCEM and M29.

Elem.	Correlation (R^2) (13 Runs)	Correlation (R^2) (11 Runs)[1]	Spike Ratio[2] High Runs: Low Runs		
			MSE	M29	XCEM
Ni	0.9482	0.9753	2.57	2.52	2.12
Pb	0.9966	0.7623	NS	NS	NS
Sb	0.9609	0.9682	2.52	2.56	2.51
Zn	0.9766	0.9738	2.57	2.54	2.50
Hg	0.4002	0.3526	3.09	3.11	2.17

NS: Not spiked
[1] Runs 3 through 13
[2] High runs are runs 3-7; low runs are runs 8-13

Response to Changes in Metal Concentration

MSE-TA spiked Ni, Sb, Zn, and Hg at two distinct concentration levels. The theoretical ratio, based on spiking, between high and low concentration runs ranged from 2.52 for Sb to 3.09 for Hg (Table 9). Since these four elements are typically not found in the stack gas in significant quantities, it was expected that the theoretical ratio would be measured by both the M29 and XCEM. Except for the XCEM Hg concentrations, both the XCEM and M29 ratios were in very good agreement with the theoretical ratio of concentrations. This agreement, along with the high correlation coefficients, indicates that the XCEM was precisely and consistently measuring Ni, Sb, Zn, and Pb and was responsive to changing concentrations. In addition, the XCEM's response to changes in the Pb concentration, which changed by almost two orders of magnitude, was consistent with the M29 results illustrated in Figure 8.

Relative Accuracy

Table 10 shows XCEM, M29 reported concentrations, and MSE-predicted spike concentrations. The RA of the XCEM with respect to the M29 was determined using PS-10 criteria. Of the 13 M29 runs, 11 were used to calculate RA and average concentrations. During runs 1 and 2, the incinerator experienced problems with a faulty bypass valve, which led to extremely high Pb concentrations (1,000 to 3,000 µg/dscm). Although the XCEM tracked the problem, and was in fact used to identify and rectify the problem, it was not felt that these conditions represented the typical operating conditions of the plant. For this reason, runs 1 and 2 were not used to calculate RA and average concentrations.

Since 11 valid reference method test runs were completed, the RA procedure stated in PS-10 allowed for omission of up to two additional runs from the RA calculation. Table 11 shows the RA for all 11 runs and the best 9 runs. In general, with the exception of Pb, the omission of two additional runs did not significantly affect RA calculations.

Table 10. XCEM measured, M29 measured, and MSE-predicted metal concentrations (μg/dscm) during TEAD validation testing.

Run No.	As			Ba			Cd			Cr			Hg			Ni			Pb			Sb			Zn		
	XC	M29	MSE	XC	M29	MSE	XC	M29	MSE	XC	M29	MSE	XC	M29	MSE	XC	M29	MSE	XC	M29	MSE	XC	M29	MSE	XC	M29	MSE
1	23	11	12	187	256	230	27	30	32	2	4	3	194	292	285	462	385	474	1,240	1,618	NS	372	565	546	333	467	479
2	16	11	12	224	298	223	27	38	31	2	4	3	229	276	281	410	401	466	2,690	3,242	NS	375	629	530	335	471	472
3	13	9	11	154	201	206	25	30	30	3	4	3	260	286	281	406	377	469	73	84	NS	351	535	516	334	418	469
4	16	12	14	161	255	200	30	34	36	5	7	5	76	318	269	422	452	448	62	64	NS	361	643	499	340	495	448
5	16	12	14	175	241	199	34	35	35	6	6	5	110	318	267	438	418	444	47	46	NS	381	627	497	354	454	444
6	14	12	14	170	271	198	33	35	35	6	6	5	152	319	270	443	473	450	41	45	NS	384	694	495	363	512	450
7	17	12	14	174	279	195	32	34	36	6	6	5	132	318	270	461	486	450	40	52	NS	383	712	489	367	540	450
8	17	12	14	148	262	200	32	35	36	5	7	5	27	104	92	210	206	184	229	198	NS	134	272	200	146	219	184
9	17	11.37	14.33	162	223	198	32	35	36	5	7	5	54	105	90	210	178	179	166	77	NS	145	237	198	146	193	179
10	18	11.42	14.16	167	214	197	34	34	35	6	6	5	91	101	88	206	161	175	143	84	NS	147	221	197	143	175	175
11	16	11.43	14.16	163	233	197	30	33	35	5	6	5	94	101	87	201	186	175	96	54	NS	145	256	197	143	201	175
12	17	9	11	182	214	200	27	28	26	4	5	4	62	108	88	218	161	177	195	187	NS	156	236	200	150	181	177
13	18	12	14	165	248	195	35	36	36	6	6	5	77	84	82	186	156	163	116	109	NS	159	286	195	118	173	163
Avg. (Runs 3-13)	**16**	**11**	**14**	**166**	**240**	**199**	**31**	**33**	**34**	**5**	**6**	**5**	**103**	**197**	**171**	**309**	**296**	**301**	**110**	**91**		**250**	**429**	**335**	**237**	**324**	**301**

XC: XCEM

NS: Not spiked

R5-2014-010471000365

Table 11. Relative accuracy and correlations.

Elem.	Avg. M29 Conc. (µg/dscm)	Avg. XC Conc. (µg/dscm)	Avg. MSE predicted Conc. (µg/dscm)	%RA (Runs 3-13)	%RA (9 Runs)	Notes
Cd	33	31	34	10	8	Met RA criterion.
Cr	6	5.2	5.0	19	15	Met RA criterion.
Ni	296	309	301	11	11	Met RA criterion.
Pb	91	110	NS	45	22	
Ba	240	166	199	39	37	Spiked with Sb. XC is consistently low.
Sb	429	250	335	58	55	Spiked with Ba. XC is consistently low.
Zn	324	237	301	37	35	Potential calibration error. XC is consistently low.
As	11.3	16.4	13.6	55	48	XC had correctable Pb interference for As.
Hg	197	103	171	78	68	Consistent pattern of increase throughout day until concentration approaches M29 value.

NS: Not spiked
XC: XCEM

Cadmium, chromium, and nickel

The XCEM and M29 reported concentrations for Cd, Cr, and Ni are in good agreement. The average XCEM concentrations for these three metals were 31, 5.2, and 309 µg/dscm, respectively, while the M29 average concentrations were 33, 6.0, and 354 µg/dscm. The high correlation between the two methods is reflected in the low relative accuracies of 10 percent for Cd, 19 percent for Cr, and 11 percent for Ni. All three elements would have met the RA requirements of the draft PS-10.

The RA for Cr would have been significantly improved if not for a high bias in the M29 results due to protocol assumptions and high analytical uncertainties in M29 back-half concentrations. EPA M29 protocol requires the assumption that the detection limit be used for the concentration when the concentration is in fact below the detection limit. In most cases, the detection limit is low relative to the measured concentrations. In the case of Cr, however, it is almost 20 percent of the total Cr found in the M29 sample train.

Lead

The average reported XCEM Pb concentration was 110 µg/dscm for runs 3 through 13, while the average M29 concentration was 91 µg/dscm. In general, the XCEM and M29 concentrations were in good agreement. On 16 May, however, both the XCEM and M29 methods reported higher Pb concentration at the start of the day than was observed on 15 May. The XCEM reported a consistent gradual decline in concentrations throughout the day while M29 showed a more rapid decrease in concentration (Figure 10). Although the average XCEM and M29 concentrations differed by only about 2 percent for runs 3, 4, 5, 6, 7, 8, 12, and 13, the large difference found in runs 9, 10, and 11 was enough to raise the RA from about 14 percent for these 8 runs to almost 45 percent for all 11 runs. PS-10 allows for 2 of the 11 runs to be dropped. This would have given an RA of 22 percent for the XCEM Pb concentrations.

It is not known why the XCEM and M29 differed on 16 May. The XCEM was able to rapidly transition from much higher concentrations during the first two runs to a much lower concentration during the third run on 14 May and was in good agreement with M29 for the third run on that day. The 14 May XCEM/M29 comparisons indicate that the XCEM is responsive to rapid changes in Pb concentration and is resistant to sample line contamination, while M29 data showed good precision and QA/QC for 16 May. The XCEM has historically measured Pb accurately with RAs below 20 percent during the MSE-TA test (Bryson 2000) and the laboratory test in 2000 (Hay et al. 2005).

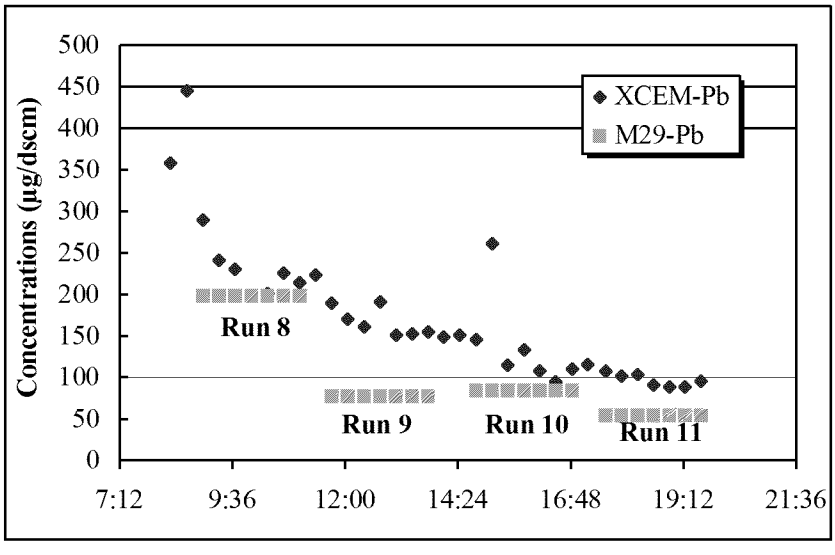

Figure 10. XCEM and M29 lead concentrations during runs 8–11.

R5-2014-0104710000365

Barium and antimony

Barium and antimony were spiked in the same solution and exhibited similar behavior during M29 testing. For both metals, the average XCEM concentrations were significantly lower than the M29 reported concentration (30 percent lower for Ba and 40 percent lower for Sb).

The XCEM to M29 ratios for Ba and Sb were 0.70 ± 0.08 and 0.59 ± .06, respectively (Figure 11). The consistent difference in concentrations is reflected in the XCEM and M29 ability to measure Sb at two concentration levels. Antimony was spiked at two different levels that were theoretically 2.52-fold different in concentration. M29 measured a 2.56 fold difference between high and low Sb concentrations while the XCEM showed a similar change with a 2.51 ratio. The XCEM and M29 Sb correlation is reflected in a high R^2 value of 0.96 for their correlation plot (in Figure 9).

The average M29 reported concentrations for Ba and Sb were 240 and 429 µg/m³ respectively, which is more than 20 percent higher than the predicted maximum stack concentration based on stack spiking (Table 11). The XCEM Ba and Sb concentrations compared favorably to the MSE-predicted concentrations. The XCEM has an RA of less than 20 percent for Ba when compared directly with the MSE-predicted concentrations.

The differences between the XCEM and predicted concentrations are believed to be due to particulate loss in the unheated XCEM transport line and calibration errors.

R5-2014-0104710000365

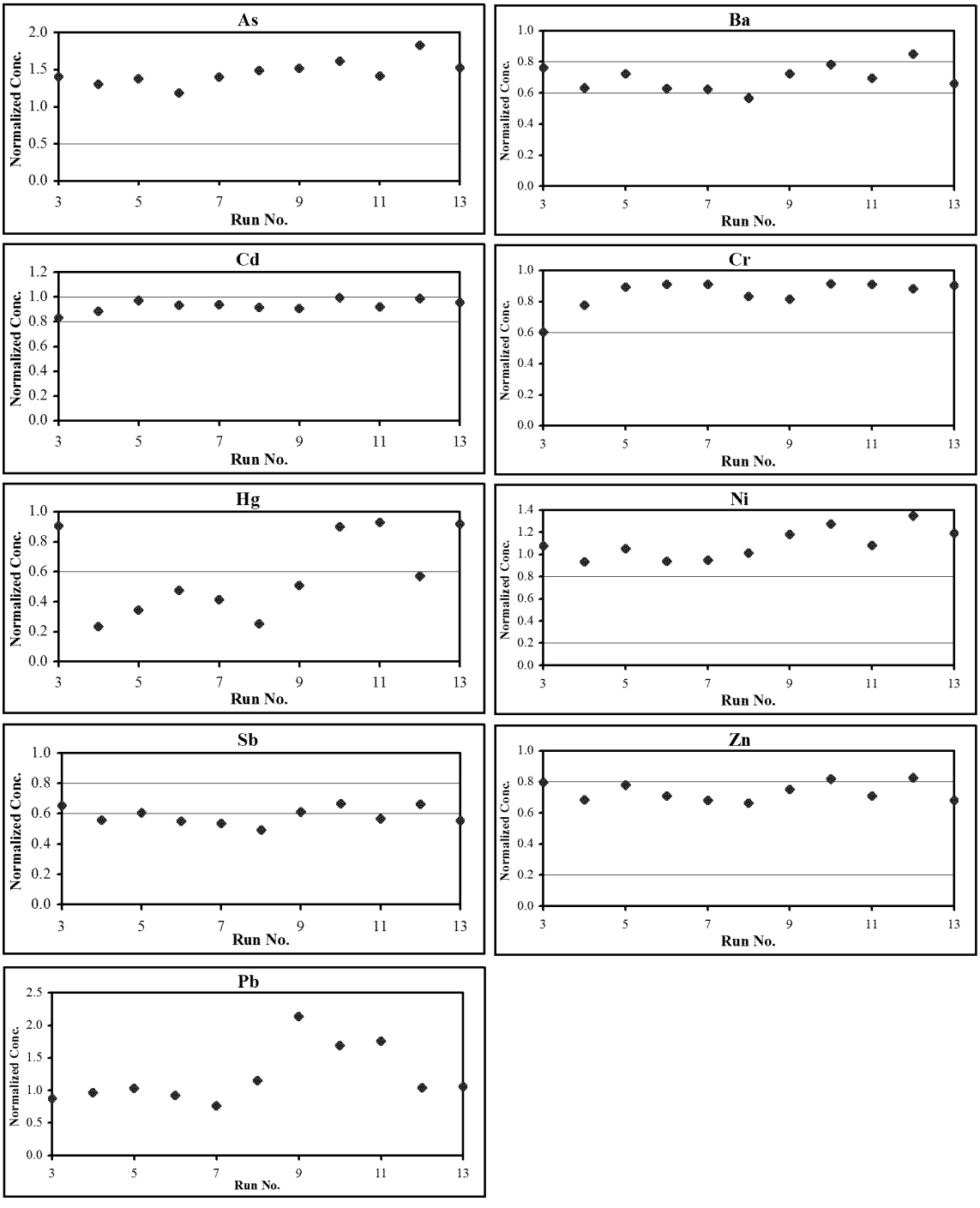

Figure 11. Ratio of XCEM to M29 concentrations during validation testing.

Zinc

Like Ba and Sb, the XCEM Zn concentrations were consistently lower than the M29 concentrations by about 30 percent. XCEM Zn concentrations were highly correlated with M29 (Figure 9) with an R^2 value of 0.98. Zinc was spiked at a high concentration level for runs 1 through 7 and a 2.57 fold lower level for runs 8 to 13. The XCEM was responsive to this difference showing a 2.50 concentration multiplier between the average high and low concentrations, which is in good agreement with the M29 ratio of 2.54.

Unlike Ba and Sb, however, the other elements spiked with Zn showed no indication of uniform loss during transport. Nickel met the PS-10 RA requirements and XCEM Ni concentrations were slightly higher than M29 Ni concentrations. Mercury, as discussed earlier, had potential transport problems to the XCEM under cooler conditions but was approximately equal to M29 concentrations for 4 of the 11 runs. Since the elements spiked in the same solution with Zn did not show systematic loss during transport, it is believed that the low Zn concentrations are not simply a function of transport problems.

CES calibrated the XCEM using thin film standards produced by MicroMatter Inc. (Deer Harbor, WA) and a select few National Institute of Standards and Technology (NIST) traceable standards. During calibration, the NIST standards and MicroMatter standards did not agree for Zn. A decision was made to use the NIST standard, which produced significantly lower reported Zn values. Following testing, it was determined that the NIST Zn standard is not in agreement with the NIST Cu standard and may be incorrect. It is believed that the Zn differences are primarily a function of this calibration error. Use of the MicroMatter calibration standard instead of the NIST standard would have given XCEM concentrations about 15 percent higher.

Arsenic

In general, the XCEM As concentrations were consistently higher than the predicted (spiked) and measured M29 concentrations. During M29 testing, it was observed that Pb concentrations were highly correlated with As (Figure 12). Since no significant As was expected in the background stack gas concentration and the As was spiked at a constant rate, the observed correlation was determined to be due to an XRF spectral interference. Arsenic concentrations are established using a Ka line, which is overlapped by the La line of Pb. For this reason, in XRF analysis, high Pb concentrations can interfere with As measurements, although the reverse is not true.

As a first cut, the interference impact was estimated using the simple linear regression shown in Figure 12. That is, about 5.4 percent of the Pb concentration was being added to the measured As concentration. CES adjusted the As numbers accordingly prior to receiving M29 data. Even with this first order adjustment, the XCEM final reported As concentrations were still higher than the M29 and predicted concentrations with the greatest deviations occurring during high Pb runs. Overall, the average final reported XCEM concentration was 16.3 µg/dscm while the average M29 concentration was 11.3 µg/dscm.

Since the XCEM saves each XRF spectrum, it was possible to review individual spectra and adjust for the As/Pb interference using a second spectral resolution approach. This task was completed after receiving the M29 data for runs 8 through 11 on 16 May. These adjusted XCEM results based on this second spectral analysis approach were within 4 percent of the M29 results.

It is believed that a change in the spectral resolution approach will resolve the Pb/As overlap problem. The XRF can be calibrated using a variety of methods that will take into account the Pb/As interference. For example, during the fall 2000 tests, a calibration method was used that contained both arsenic and Pb. No As/Pb interference was observed during these tests (Hay et al. 2005).

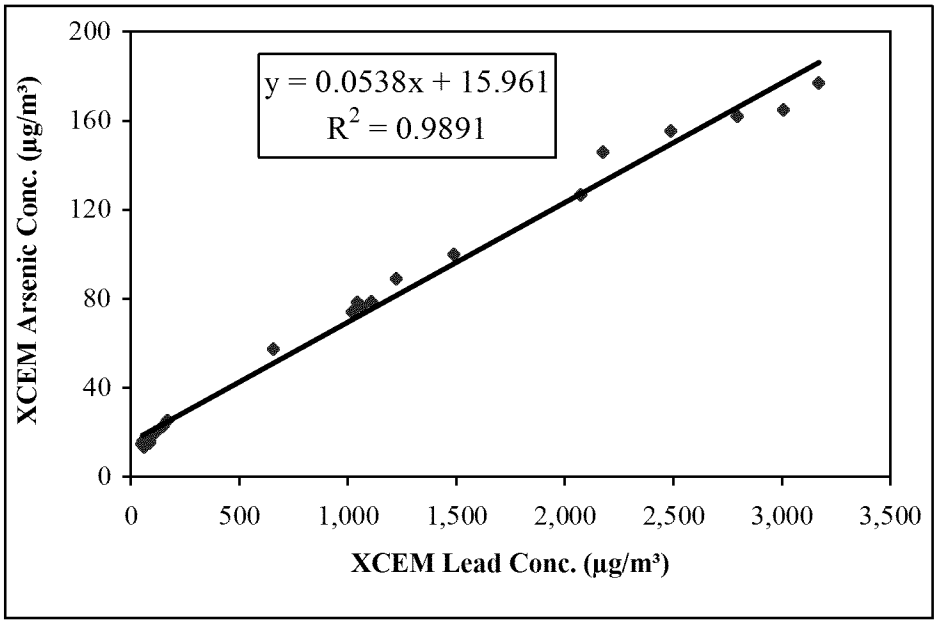

Figure 12. Uncorrected XCEM As concentrations versus XCEM Pb concentrations.

Mercury

As discussed earlier, the XCEM to M29 Hg ratios varied from run to run. At the beginning of each test day, the XCEM reported low Hg concentrations relative to M29. As the day progressed, the XCEM concentration would gradually increase until it approximated M29 reported concentrations. The pattern suggests that the transport line from the stack to the XCEM needed to be heated to a higher temperature to improve transmission efficiency. The use of a heat-traced transport line should improve Hg transmission efficiency.

Interestingly, more than 98 percent of the Hg measured by M29 passed through the filter and was collected in the back half of the sample train indicating that the vast majority of the Hg was in the vapor phase. Since the XCEM had good comparisons to M29 on at least four runs (3, 10, 11, and 13), the test indicates that the XCEM was able to efficiently trap and measure Hg as a vapor.

Precision

Precision was calculated in terms of the percent relative standard deviation (RSD) of a series of XCEM measurements made during relatively stable operation of the TEAD incinerator, with metals injected at a relatively constant rate. This precision reflects not only the XCEM variability, but also the variability in the stack concentrations, spiking rate, and flow variability.

Method 29 dual sample train precision

During testing, CHPPM ran dual M29 sample trains. Percent differences between the two trains are shown in Table 12. Overall, the average metal concentration agreement between the M29 trains was about 6 percent (CHPPM 2001). This result is significantly better than the typical agreement between trains, which is on the order of 15 percent (EPA 1999). This better-than-typical agreement indicates that M29 sampling and analysis were conducted in a precise manner.

Method 29 vs. XCEM precision

The spike injection rate was altered on the first day of testing, 14 May, to ensure spiked emissions were within the site permit limitations. On 17 May, stack conditions were not stable following stack repairs. However, MSE-TA and TEAD reported reasonably stable conditions on 15 and 16 May and the spiking precision was estimated at 2 percent. For this reason, the eight runs on 15 and 16 May were used for precision calculations.

R5-2014-0104710000365

The average M29 and XCEM precisions for the eight spiked elements on 15 to 16 May are listed in Table 13. The average M29 precision for these runs was about 6 percent, while the XCEM average precision was about 10 percent. The XCEM precision, however, was heavily influenced by the highly variable Hg results. For the non-Hg elements, the precision of the XCEM was 3.7 percent, while the average M29 precision for the same group of elements was 6.8 percent.

The XCEM also measures Pd with every sample. The average XCEM Pd concentration was 25 ± 0.6 µg, which gives a precision of about 2.5 percent. Palladium concentrations reflect XRF precision, but are independent of flow, spiking, and sampling variability.

Overall then, the XCEM performed in a very consistent manner and exhibited precision on the same order as or slightly better than M29 for all elements except Hg.

Table 12. Percent differences between M29 sample trains.[1]

Run	As	Ba	Cd	Cr	Hg	Ni	Pb	Sb	Zn	Avg. % Diff
1	9	-6	-2	7	2	3	-19	-4	-9	**7**
2	1	15	9	5	-3	0	0	-1	-1	**4**
3	-2	-5	0	8	3	-1	11	1	5	**4**
4	-2	-6	-8	-26	3	-5	5	-4	-2	**7**
5	-9	-12	-6	-15	1	-11	-3	-11	-9	**9**
6	0	-8	1	0	0	-2	6	-9	-5	**3**
7	3	-8	-3	-2	0	-6	-1	-9	-7	**4**
8	1	-3	-5	-4	4	-9	-14	-11	-10	**7**
9	6	-8	-3	12	0	9	7	3	7	**6**
10	0	6	-5	-5	-2	11	2	5	5	**5**
11	-4	-3	-5	-5	-1	-10	-1	-10	-13	**6**
12	6	14	8	8	0	11	11	5	12	**8**
13	-2	-14	-1	-1	1	-11	-2	-14	-9	**6**
Avg. % Diff.	**4**	**8**	**4**	**8**	**2**	**7**	**6**	**7**	**7**	**6**

[1] Average percent difference is determined by averaging the absolute value of the difference between sample trains.

Table 13. XCEM and M29 precision.

Elem.	M29 Runs	Avg. M29 Conc. (µg/dscm)	M29 % RSD	Avg. XC Conc. (µg/dscm)	XC % RSD (By Run)
As	4-11	12	2.3	16	7.6
Ba	4-11	247	9.4	165	5.2
Cd	4-11	34	2.3	32	4.5
Cr	4-11	6	5.7	6	2.6
Hg (high)	4-7	211	0.2	92	35.4
Hg (low)	8-11	103	1.9	67	48.4
Ni (high)	4-7	457	6.5	438	3.6
Ni (low)	8-11	183	10.1	207	2.0
Sb (high)	4-7	669	6.1	375	2.9
Sb (low)	8-11	246	9.0	143	4.2
Zn (high)	4-7	500	7.2	354	3.4
Zn (low)	8-11	197	9.2	144	1.2
Avg. (All elem.)			**5.8**		**10.1**
Avg. (No Hg)			**6.8**		**3.7**

Low-Level Metal Response

Low-level metal response was determined by comparison of M29 and XCEM-reported Cr and As concentrations. Neither of these elements is found in significant quantities in TEAD stack emissions and both are regulated to low levels under the site-based RCRA limitations. Both elements were spiked as particulates by MSE-TA at low concentrations with typical Cr stack concentrations in the 5 µg/dscm range and As in the 14 µg/dscm range.

The XCEM accurately measured Cr relative to M29 with an RA of 19 percent. The average XCEM Cr concentration was 5.2 ± 0.9 µg/m³ while the M29 average was 6.0 ± 0.8 µg/m³. The M29 concentrations reported the detection limit for the back half when no Cr was measured, which occurred for more than half of the samples. Since the M29 back half detection limit was about 0.5 µg/m³, the M29 concentrations were biased high by at least 10 percent. Correction for the M29 back-half detection limit improves the RA to better than 10 percent. This consistent agreement between the two methods demonstrates the capability of the XCEM to measure metals at low concentrations even in the presence of high concentrations of interfering elements such as Ba.

As discussed earlier, the XCEM As concentrations were biased by Pb interference. For this reason, the XCEM As concentrations were routinely higher than the M29 concentrations.

Bias

Bias between the two M29 sampling trains and the M29/XCEM data was determined using an EPA Method 301 approach (EPA 1992). The results are tested for statistically significant bias by calculating the t-statistic and determining if the mean of the differences between the two sampling trains is significant at the 80-percent confidence level. The t-statistic is calculated by finding the standard deviation of the differences between the two sampling trains.

$$SD_d = \sqrt{\frac{\sum (d_i - d_m)^2}{(n-1)}} \qquad \textbf{[Eq 4]}$$

where:

d_i = the difference between the two sample train values
d_m = mean of the d_i values
n = number of paired samples

Using the standard deviation determined in Equation 4, the t-statistic is then calculated as follows:

$$t = \frac{|d_m|}{\left[\frac{SD_d}{\sqrt{n}}\right]} \qquad \textbf{[Eq 5]}$$

Based on EPA criteria, a statistically significant bias in a data set exists if the t-statistic value is greater than a critical value (0.88 for 11 runs).

Using Equations 4 and 5 and EPA's critical value for 11 runs, it was determined that M29 experienced statistically significant bias between the paired sample trains for Ba, Cd, Cr, Hg, Ni, Sb, and Zn. However, the M29 bias was small, on the order of 3 to 6 percent. Furthermore, the bias was not consistent by element with sample Train A being higher for Cr and Hg while Train B was slightly higher for As, Ba, Cd, Ni, Sb, and Zn. Overall, the M29 sample trains had an average absolute percent difference of about 6 percent (Table 9). Since the M29 bias for individual elements was relatively small and no consistent differences between sample trains was noted, it was determined that the average M29 concentration would be used for comparison purposes and no correction would be taken to compensate for bias.

Relative to M29, the XCEM showed significant bias for all elements (Table 14). This bias is believed to be a product of XCEM transport and calibration problems. Method 301 outlines a procedure for determining correction factors that can be applied when bias is present. If the Method 301 correction factor had been applied to the XCEM concentrations, the XCEM would have met the 20 percent RA criterion for all of the elements except Hg. Although this method shows the existence of a high level of correlation, it is important to note that the XCEM correction factors are outside of the acceptable range for validation of Pb, Ba, Sb, Zn, As, and Hg.

Table 14. Method 301 bias and correction factor comparison.

Element	T-Stat	Significant Bias	Correction Factor	RA with Corr. Factor (Runs 3-13)	Corrected RA Meets PS-10
Cd	5.33	Yes	1.08	3.9	Yes
Cr	6.41	Yes	1.17	6.3	Yes
Ni	1.27	Yes	0.96	8.0	Yes
Pb	1.87	Yes	0.83	20.2	Yes[1]
Ba	9.59	Yes	1.46	8.7	Yes
Sb	6.17	Yes	1.73	6.5	Yes
Zn	5.64	Yes	1.38	6.1	Yes
As	11.75	Yes	0.69	7.8	Yes
Hg	3.44	Yes	1.91	35.9	No

[1] Using only nine runs as suggested in PS-10, Pb RA would have been 14 percent.

Summary

The XCEM was constructed, installed at the TEAD incinerator, and tested against M29. The primary objective was to meet the proposed requirements of PS-10. Following is a list of the individual requirements and discussion of the performance of the XCEM:

1. *Response time and reporting time:* The XCEM had a response time of 20 minutes, meeting the PS-10 criterion for batch CEMs. It experienced no mechanical problems and had an effective up-time of 100 percent.
2. *QA:* The XCEM showed a calibration drift of less than 0.5 percent and QA precision of about 2 percent for daily zero and upscale checks.
3. *Relative accuracy:*
   a. The XCEM met PS-10 accuracy criteria for Cd, Cr, and Ni by having relative accuracies that were less than 20 percent.

b. The XCEM did not meet the Pb accuracy criterion with an RA of 22 percent.
c. The reported XCEM concentrations were uniformly high for As due to a spectral resolution problem.
d. The XCEM was consistently low for Zn. The Zn differences are believed to be due to an incorrect XCEM calibration standard that lowered the XCEM concentrations by about 15 percent.
e. The XCEM was also consistently low for Ba and Sb. These differences are believed to be a function of transport or calibration problems.
f. The XCEM did not successfully measure Hg, which exhibited a concentration pattern that suggests loss to the unheated sample transport line.
g. The XCEM had a correlation (r^2) of better than 0.95 for three (Ni, Sb, Zn) of the four elements that were spiked at varying concentrations.

In addition, during the tests the XCEM functioned in a completely automated manner and automatically recorded concentrations, temperatures, flow rates, and QA data. It also showed a precision of better than 4 percent for periods when spiking and stack conditions were held relatively constant.

An analysis of reported concentrations using EPA Method 301 correction factors indicates that the XCEM would meet the 20 percent RA criterion for all elements except Hg, once the bias is taken into account. However, the correction factors are outside the acceptable range for validation. Table 15 summarizes the results relative to PS-10.

Table 15. Summary of XCEM performance relative to proposed PS-10 requirements.

Test Goal	Met Criterion?	Discussion
Sampling and Response Time	Yes	Exhibited a 100% up-time for test. Sampled for greater than 99.5% of the time. Reported time averaged concentrations every 20 minutes with a 20-minute lag between sampling and reporting.
QA	Yes	The XCEM exhibited a precision of 1 to 2% for zero drift. The XRF calibration drift was less than 0.5% for the 4 days of testing.
RA	Yes for 3 No for 6 elements	Met 20% RA criteria for Cd, Cr, and Ni. Had a 22% RA for Pb. Was systematically biased for Ba, Sb, Zn, and As. Did not successfully measure Hg. For response to change in concentration, had correlation (r^2) of 0.95 or better for Ni, Sb, and Zn. Underlined elements are regulated elements typically found in the Tooele feedstream.

R5-2014-0104710000365

3 Transport and Calibration Improvements

During the M29 comparison tests of May 2001, the XCEM met the PS-10 criteria for QA and sampling and response time, but only met the RA criterion for three elements (Cr, Cd, and Ni). 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 RA.

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. This chapter discusses the changes to the transport line, calibration, and test results.

Transport Line Changes

The initial transport line used by the XCEM at TEAD was insulated, but not heat traced. The line, which extended horizontally 20 ft, showed problems with Hg transport. During May 2001 testing, XCEM Hg concentrations were lower than M29 values at the beginning of the day when temperatures were lower, but as the line temperature increased, the XCEM Hg concentrations approached M29 results. For this reason, it was determined that the XCEM required a heated transport line.

In March 2002 the XCEM shelter was moved to a location that required only 13 ft of horizontal transport. Following the move, the line was heat traced, insulated, and maintained at 220 ºF. In addition, a shrouded probe was installed. The shrouded probe, manufactured by Anderson Instruments, has been shown to minimize the impact of variations in stack velocity on deviations from isokinetic sampling (McFarland and Rodgers 1993). The combined effect of these changes was to minimize Hg and particulate loss in the sample line.

R5-2014-0104710000365

Recalibration

During the week of 8 April 2002, CES recalibrated the instrument using thin-film MicroMatter standards. The thin-film standards are developed by flashing the metal of interest onto a nuclepore filter, resulting in a known concentration of metal in micrograms per square centimeter (µg/cm²). The XRF unit used by the XCEM had not been calibrated since August 2001. Before recalibrating, CES analyzed the MicroMatter standards (previously purchased by the Army as unknowns) to evaluate the XRF's stability. The XRF reported values within 10 percent of the calibration standards, which indicated that it had maintained good stability for 9 months and would not have needed recalibration under normal operating conditions.

Following the initial check, several changes were made to the calibration procedure to improve spectral deconvolution. These changes included:

- Development of a representative filter tape background reference spectra
- Subtraction of the filter tape background spectra
- Development of better pure element reference spectra
- Inclusion of additional elements as background spectra to correct for potential interferences.

Following recalibration, the Army MicroMatter standards were again evaluated as unknowns. The standards were within 1.5 percent of the listed values for all elements except Sb (6 percent) and Ba (15 percent). The accuracy of the Army MicroMatter standards was in question, so they were compared to CES MicroMatter standards at the CES laboratory. Some inconsistencies for Cd and Pb were noted between the Army and the CES MicroMatter standards. They were also compared with standards from NIST. The results from the analysis of the NIST and CES MicroMatter standards were compared with the Army MicroMatter standards, and it was determined that the Army standards for Cd and Pb were high by 12 percent and low by 4 percent, respectively. The XRF calibration was adjusted accordingly.

Summary of Transport and Calibration Evaluations

Changes to the transport line were tested by comparing XCEM concentrations to concentrations based upon stack spiking estimates and an in-stack EPA Reference Method 17 (M17) filter. Overall, no measurable loss of particulates in the improved XCEM transport line was observed. The calibration was tested using a

R5-2014-0104710000365

Quantitative Spike Injection System (QSIS). It was determined that the elemental concentrations were being reported within their expected uncertainties for all elements except Cd and Ag. Appendix C gives descriptions and detailed results of these tests.

R5-2014-0104710000365

4 M29 Comparison Testing of XCEM 2002

In May 2002 a new series of M29 tests were conducted to evaluate the measurement capabilities of the improved XCEM. The test objective was to compare M29 and the XCEM and determine the XCEM RAs. The testing was conducted at TEAD with a test plan similar to the plan used in the 2001 M29 comparison tests. Ten metals were measured by M29 and the XCEM. This chapter presents the results of the M29 sampling, predicted concentrations based on the spiking, and the XCEM sampling. Also presented: a calibration evaluation based on the reevaluation of the XCEM filters, a discussion of the precision of the three concentration determinations, and a detailed discussion of the M29 comparison.

Results

Method 29 Concentrations

Method 29 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 (CHPPM 2002). As shown in Table 16, more than 90 percent of the paired M29 concentrations were within 10 percent of each other. Of the 11 reported concentrations that were not within 10 percent, 9 were measurements of Sn. Method 29 has not been approved for Sn (EPA 1992). Tin is not a regulated metal, but measuring it is useful to TEAD for identifying deactivated munitions.

Overall, train A was higher than train B by about 3 percent with about 78 percent 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.

Method 29 data used for comparison to the XCEM is the same as reported in the M29 report (CHPPM 2002) with the exception of a 1–3 percent correction compensating for the laboratory's inadvertent subtraction of an estimated blank concentration when the blank concentrations were below the method-reporting limit.*

* Personal communication: Robert Weidenfeld, Severen Trent Lab, with John Cooper, CES, 9 July 2002.

Table 16. M29 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

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 concentrations, which were 17, 15, and 8 percent, respectively. For Pb, however, the background accounted for 100 percent of the Pb in runs 1–5 and 35 percent of the Pb in runs 6–12.

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 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 percent of MSE-TA's estimates for all elements except As,

which was 23 percent lower according to HKM than reported by MSE-TA. No adjustments were made to MSE-TA reported data. The potential impact of the As difference is discussed in a report by Cooper et al. (2002).

Measurements of stack flow by CHPPM were cross-checked with the stack continuous velocity monitor for accuracy and were found to be within 6 percent of each other (Table 17). 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.* For this reason, the CHPPM flows were used to calculate the predicted concentrations.

Table 17. APE-1236 stack flow rates during M29 testing.

Run	TEAD stack monitor (dscm/hr)	M29A (dscm/hr)	M29B (dscm/hr)	Avg. CHPPM M29 (dscm/hr)	TEAD stack/ Avg. M29 (%)
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	4,060	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

Background metal concentration

TEAD incinerated 20 mm TPM55A2 bullets during all 12 M29 runs. This ammunition, 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 18 shows XCEM results for elements measured on 13 and 15 May while the 20 mm bullets were being burned and MSE-TA was not spiking into the stack. The 13 May metal concentrations were significantly higher than

* Personal communication: Mike Pattison, U.S. Army CHPPM, with Bruce Johnsen, CES, June 2002.

the 15 May concentrations, which 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 (1 µg/dscm) and were reported as 0 µg/dscm.

Table 18. APE-1236 stack concentrations (µg/dscm) with munitions incineration but no spiking.

Date	XCEM 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
	Average	**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
	Average	**19.4**	**1.7**	**19.3**	**6.7**	**102**

Use of Sn as a surrogate for background metals

Figure 13 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 13. Figure 14 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 19.

R5-2014-0104710000365

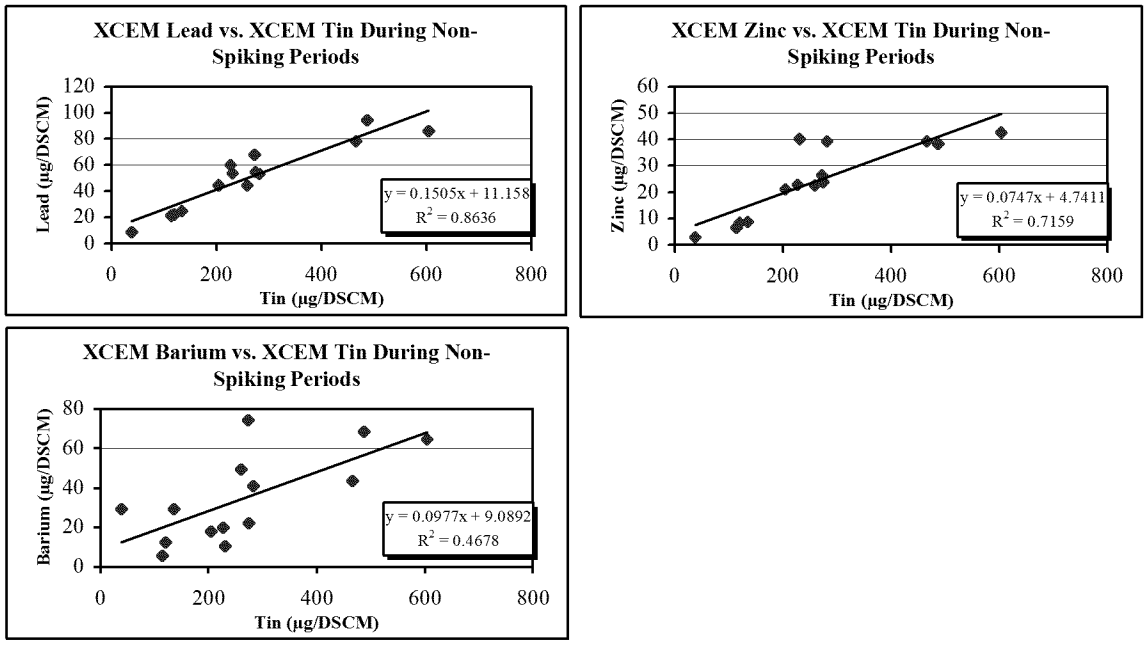

Figure 13. Correlation between Sn and other APE-1236 metals with munitions burning and no spiking.

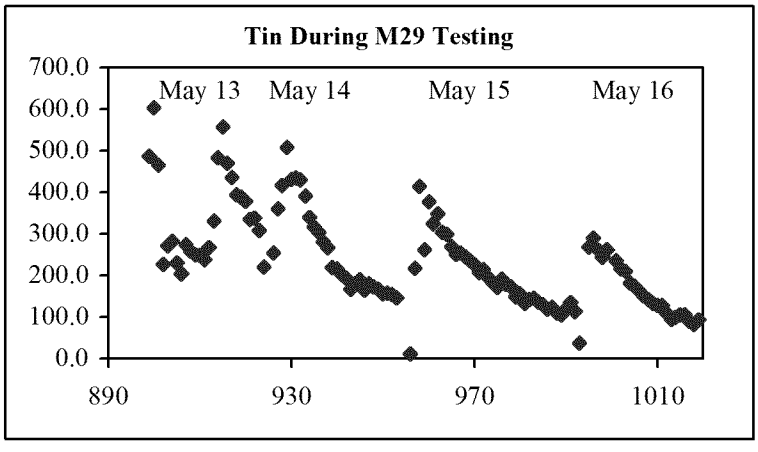

Figure 14. XCEM tin measurements during M29 testing.

R5-2014-0104710000365

XCEM Concentrations

XCEM concentrations were determined every 20 minutes for Pb, Cd, Cr, As, Ni, Hg, Ba, Sb, Zn, and Sn (Table 20). A Pd rod is permanently mounted in the XRF detection area and is measured with every sample. The consistency of the Pd concentrations provides QA of the instruments stability during M29 testing, the XCEM successfully carried out 120 runs with only 2 runs falling outside of the Pd QA criterion due to air-conditioning problems. This represents an uptime of 98 percent.

Table 19. Predicted stack concentrations (µg/dscm) based on MSE-TA spiking and background estimates.

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 20. XCEM concentrations.

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

R5-2014-010471000365

Table 20 (Cont'd). XCEM concentrations.

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

R5-2014-0104710000365

Table 20 (Cont'd). XCEM concentrations.

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

R5-2014-010471000365

Table 20 (Cont'd). XCEM concentrations.

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

R5-2014-010471000365

The XCEM data were then averaged for each M29 run using equation 7:

$$C_i = \frac{\sum_{j=1}^{n} C_{ij} t_j}{\sum t_j} \qquad \textbf{[Eq 7]}$$

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. It was observed that Sb, Ba, and Hg calibration factors were too high relative to the calibration standards by 15, 15, and 7 percent, respectively. The calibration factors were changed prior to run 2 (Appendix D).
2. Hg calibration factors were determined to be high relative to the calibration curve by 4 percent and were changed following the M29 test (see Appendix D 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. The speck 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 16 May, which meant that the Pd QA concentration did not meet the 90–110 percent criterion for XCEM runs 1021 and 1022. These runs 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 were submitted before receiving the M29 results. No modification to the XCEM data was made after receiving M29 results.

XCEM Calibration Evaluation Using A QuanX – XRF and ICP/MS

Since XRF analysis is nondestructive, the concentrated particulate matter on the filter can be reanalyzed at a later date. 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 laboratories as well as rigorous quality control checks. The QuanX analysis was conducted approximately 6 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 are shown in Table 20 as CES Concentration (CES CONC.).

Following the reanalysis, filter spots that correlated with M29 runs 5 and 6 were combined and submitted to Columbia Analytical (Vancouver, WA) for analysis using ICP/mass spectrometry (MS). Table 21 shows results of this analysis.

Table 21. 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

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 percent, 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 5 percent.

Both the XCEM and M29 show good precision for these elements with the XCEM precision about 30 percent lower than M29 (Table 22).

Table 22. Predicted (spiked), XCEM, and M29 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.

Discussion

Regulated Elements Typically Found in the Feedstream

Although the 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 23; Be is not listed in this table because it cannot be measured by the XCEM). The XCEM successfully measured all three of the key elements and met the 20 percent RA requirements in proposed PS-10 with RAs of 4, 17, and 15 percent, respectively.

Table 23. TEAD emission limits for regulated elements.

Element	State Limit		Interim MACT Limit	Final MACT Limit	Potential to Limit Feed Rate
	g/hr	µg/dscm[1]	µg/dscm	µg/dscm	
Pb	4.3	932	240	59	Yes
Cd	0.26	56			Yes
Cr	0.04	10	97	84	Yes
As	0.11	24			No
Hg	14	3,036	130	130	No
Sb	14	3,036	NR	NR	No
Ni	930	201,740	NR	NR	No
Ba	2,400	521,243	NR	NR	No

[1] Assumes 4,635 dscm/hr based on average rate from Table 16.

NR: Not regulated; MACT: Maximum achievable control technology (rule)

Lead

Lead is the element that 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 HWC interim maximum achievable control technology (MACT) rule (EPA 1999) currently limits Pb and Cd emissions to 240 µg/dscm. The final MACT rule, which was published 20 April 2004 (FR21210) and will be in effect 3 years after it promulgates, will further limit the combined Pb and Cd emission rate to 59 µg/dscm.

Currently, Pb concentrations within the munitions are determined for each type of ordnance before incineration. Munition feed rates into the incinerator are restricted using a model that assumes that a fraction of the Pb in the munitions will be transported through the air pollution control devices and emitted from the stack. The effectiveness of the model depends 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 24 shows the Pb results for the MSE/background predicted concentrations (PRD), M29, XCEM (XC), 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 7 percent. The XCEM and M29 Pb concentrations are also highly correlated with an r^2 of 0.98 (Figure 15).

Lead in the first five M29 runs was exclusively from residual concentrations in the incinerator. Following run 5, 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 RA for the XCEM was 4.4 percent. This 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 24. Summary of Pb concentration (µg/dscm) data and ratios during M29 testing.

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**

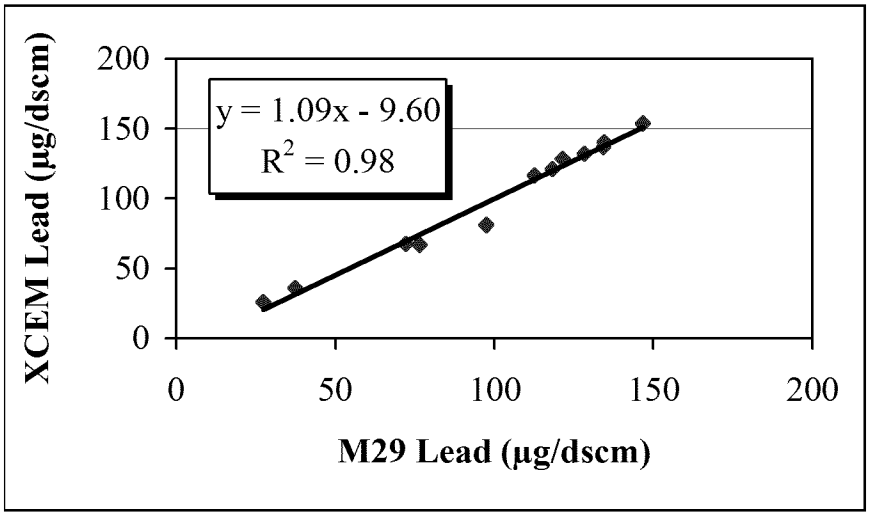

Figure 15. XCEM versus M29 lead for validation tests.

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 percent of the stack's Cd was from MSE-TA, while 20 percent was estimated to be background. Table 25 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 percent higher than M29 with an RA of 17 percent. The re-analysis of the XCEM filter tape yielded mixed results with the QuanX XRF within 3 percent of M29 and the Columbia Analytical concentrations within 4 percent 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.

R5-2014-0104710000365

Table 25. Summary of Cd concentration (µg/dscm) data and ratios during M29 testing.

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**

Chromium

The 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 percent higher than M29 at both concentration levels (Table 26). This represents a difference of about 0.5 µg/dscm. The 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.

The Cr RA was 15 percent, meeting the PS-10 criterion. Subsequent measurements of the XCEM filter tape by the CES-QuanX and ICP were within 3 percent of the M29 concentrations. The consistency of M29 with the predicted values and subsequent measurements of the XCEM filter tape suggests that the difference between the two methods is due to XCEM error.

Table 26. Summary of Cr concentration (μg/dscm) data and ratios during M29 testing.

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**

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 does not measure Be. The XCEM met PS-10 measurement criteria for Sb (20 percent) and Ba (4 percent), but was higher than M29 for As, Hg, and Ni with relative accuracies of 27, 33, and 33 percent, respectively.

Arsenic

Arsenic results are shown in Table 27. The XCEM-reported concentration was in good agreement with the post-test analysis of the filter tape by both 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. Although, as discussed earlier, the HKM analysis showed a 23 percent lower value for the calibration.

The XCEM's RA of 27 percent did not meet PS-10 criterion. Overall, the XCEM concentrations were 25 percent higher than M29 concentrations for As. Other potential sources errors for the XCEM besides calibration such as loss during transport, low filter trapping efficiency, and deposit positioning errors can be ruled out because they would result in XCEM concentrations lower than M29. It is highly possible that the differences in concentration are due to M29 errors. The XCEM was also highly correlated with M29 As (r^2=0.85) showing good responsiveness to changes in As concentration.

Table 27. Summary of As concentration (µg/dscm) data and ratios during M29 testing.

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**

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 percent 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. An earlier multi-metals monitor was certified for use at TEAD without measuring Hg (Seltzer 2000). For the current validation test, Hg was spiked by MSE-TA with results shown in Table 28.

The XCEM and M29 concentrations had acceptable agreement during runs 1–5 with the XCEM 16 percent higher than M29. Following run 5, however, the XCEM was consistently 34 percent higher than M29. It is believed that these differences are due to vaporization of particulate Hg 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 percent 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 percent in runs 1–5 to 30 percent in runs 6–12 (CHPPM 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, so it was not cooled while being shipped to California for analysis. During this time, a significant quantity of the Hg on the filter could have vaporized. Figure 16 shows the relationship between the level of Hg on the M29 filter and the percent difference between M29 and the XCEM.

The XCEM filter also showed a loss of about 30 percent 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 of vapor phase Hg on earlier tests (Cooper et al. 2000; Chapter 3) so the Hg loss seems to depend upon the quantity in the particulate phase. See Appendix D for a more detailed discussion.

Table 28. Summary of Hg concentration (µg/dscm) data and ratios during M29 testing.

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.

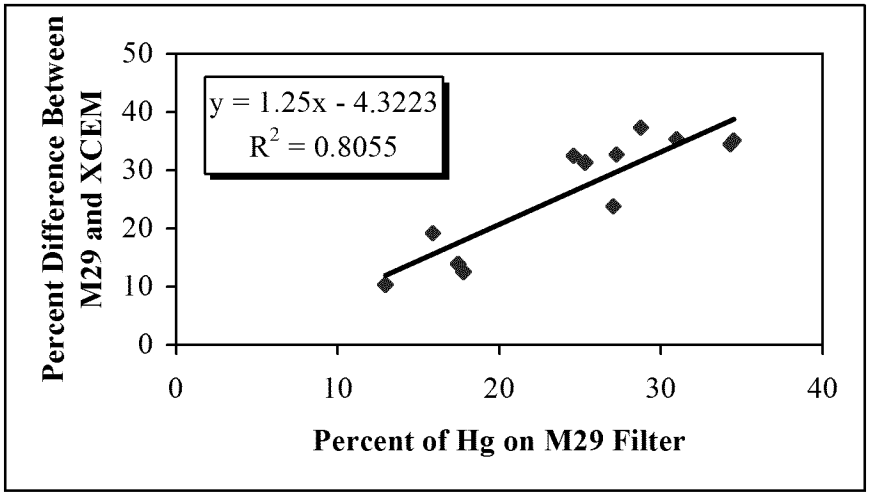

Figure 16. Percent difference between M29 and the XCEM versus percent of Hg on M29 filter.

Antimony

Antimony results are shown in Table 29. Overall, the XCEM was higher than M29 by about 18 percent, but met RA criteria with an RA of 19.9 percent. 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 percent.

Table 29. Summary of Sb concentration (µg/dscm) data and ratios during M29 testing.

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**

Nickel

Validation test results for Ni are reported in Table 30. The XCEM was about 30 percent higher than M29 and had an RA of 34 percent, which did not meet the PS-10 criterion. 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 earlier in the section on **Arsenic**, 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 30. Summary of Ni concentration (µg/dscm) data and ratios during M29 testing.

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**

Barium

Barium results for the validation tests are shown in Table 31. For Ba, the predicted concentrations, M29 results, XCEM results, and QuanX reanalysis all agree to within 10 percent with an XCEM RA of 4 percent. 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 Ba under realistic stack conditions.

Table 31. Summary of Ba concentration (µg/dscm) data and ratios during M29 testing.

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**

Nonregulated Metals

Two nonregulated 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. Zinc was spiked by MSE-TA with XCEM reported concentrations shown in Table 32.

Overall, the XCEM Zn concentrations were consistently about 40 percent 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. It is believed that the difference is primarily due to M29 errors.

Table 32. Summary of Zn concentration (µg/dscm) data and ratios during M29 testing.

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**

Summary

The XCEM met the proposed PS-10 RA requirements for the three potential emission-limiting elements found in APE-1236 that could potentially approach emission limits: Pb, Cd, and Cr. The XCEM also met the RA requirements for two other regulated metals Ba and Sb but was 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. However, calibration errors were noted for Cd, Cr, and Sb even though they met the RA requirements. 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 Cr's low concentrations when changes of only 2 µg/m^3 occurred

R5-2014-0104710000365

between runs 2 and 3. Table 33 summarizes the comparison between M29 and the XCEM.

Table 33. Summary of 2002 M29/XCEM comparison results.

Element	Average M29 Conc. (µg/dscm)	Average XCEM Conc. (µg/dscm)	Average Predicted Conc. (µg/dscm)	RA (%)	Met PS-10 RA Criterion
Pb	101	101	107	4	Yes
Cd	42.0	31.5	36.4	17	Yes
Cr	4.9	5.4	4.7	15	Yes
As	11.1	13.8	15.2	27	No
Hg	305	385	326	33	No
Sb	164	192	194	20	Yes
Ni	218	281	268	33	No
Ba	216	216	226	4	Yes
Zn	202	290	288	43	No

R5-2014-0104710000365

5 XCEM Cost and Status

Cost estimates for the Army to purchase and operate a new XCEM are discussed in this chapter. The values are presented in $1,000 units ($K) and were current in July 2004. Also presented is a summary of the continued operation of the XCEM at TEAD and status of the technology.

Cost Estimates

Capital Costs

Capital costs include:

1. **XCEM:** Includes x-ray fluorescence (XRF) spectrometer, operations manuals, extraction system, computer and control module, software, sampling system, enclosure, and calibration equipment, as well as in-house acceptance testing ($195K).

2. **Probe and Transport Line:** Includes shrouded probe, corrosion resistant transport line, heat tracing, and insulation ($10K).

3. **Shipping and Installation:** Typically includes shipping of equipment, on-site installation, onsite instrument shakedown, and final onsite calibration check. Site will be responsible for lifting and connecting transport line ($25K).

4. **Training:** Onsite training for up to six people, including training manuals, hands-on training, power point presentations, and customer support following installation ($8K).

5. **Housing:** Includes temperature-controlled housing as either an instrument grade trailer or a shelter depending upon end-user requirements ($5 to $15K).

The total estimated capital costs are between $243K and $253K.

Annual Costs

Annual costs include:

1. **Consumables:** Includes 1 year of filter tape and all other consumables. This cost will depend on usage. The low estimate is for a typical 40 hr/week schedule and the high estimate is for a 24/7 schedule ($5K to $20K).

2. **Labor:** Includes changing filter tape (1 hr once every 3 weeks for 24/7 usage; once every 2 months for 40 hr/week usage), and regular maintenance (cleaning unit and replacing filters, 6 hr every 3 months) 30–41 hr/year × $80/hr ($2.4K to $3.3K).

3. **Warranty:** Includes 1-year full-service warranty covering all parts and maintenance. Warranty includes onsite assistance as needed ($25K).

The total estimated annual costs are between $32.4K and $48.3K.

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 Pb and Zn during incineration of various munitions. TEAD stack operators also conducted tests using the XCEM in which they determined that the metals emissions could be significantly reduced by completely cutting off the bypass system during operation. Blocking the bypass duct with a metal plate resulted in a greater than 90 percent drop in metal concentrations. Using this data, TEAD was better able to understand sources of Pb in the emissions.

The XCEM has also been used by the Ammunition Equipment Directorate (AED) on their test furnace at TEAD. The continued use of the XCEM to diagnose and assist with process control indicates the value of having an installed CEM for multi-metals at TEAD. More recently (2003), AED purchased a second XCEM unit for their test furnace. It was installed during 2004.

Eli Lilly Corporation has recently (May 2004) purchased and installed an XCEM unit for one of their hazardous waste incinerators. They have submitted an Alternative Monitoring Plan (AMP) with the EPA with the intention of using the monitor for compliance purposes. The AMP should be finalized in the near

R5-2014-0104710000365

future. The monitor has been successfully integrated into the data acquisition system for the site and generates a 12-hr rolling average as required.

Improvements have been made to the technology since the original XCEM was tested. In a new XCEM (2004), the QuanX XRF instrument has been replaced with a custom XRF detection approach improving the detection limit to 0.1–0.2 µg/dscm from 1–3 µg/dscm (15-minute sample time). The monitor can now monitor up to 25 metals simultaneously. The software has been upgraded to accommodate the physical changes and to improve the ease of integration to external data acquisition systems. The physical size of the monitor has also decreased. Figure 17 shows the 2004 XCEM model from CES (X*act* is the marketing name that CES has given the XCEM). CES has developed, in the last year, a quantitative aerosol generator (QAG) that is capable of delivering a known aerosolized metal concentration. CES believes that using the QAG is a reliable, consistent, and accurate method for ensuring that the calibration has been entered correctly. The QAG is currently being evaluated by the EPA for use in compliance applications.

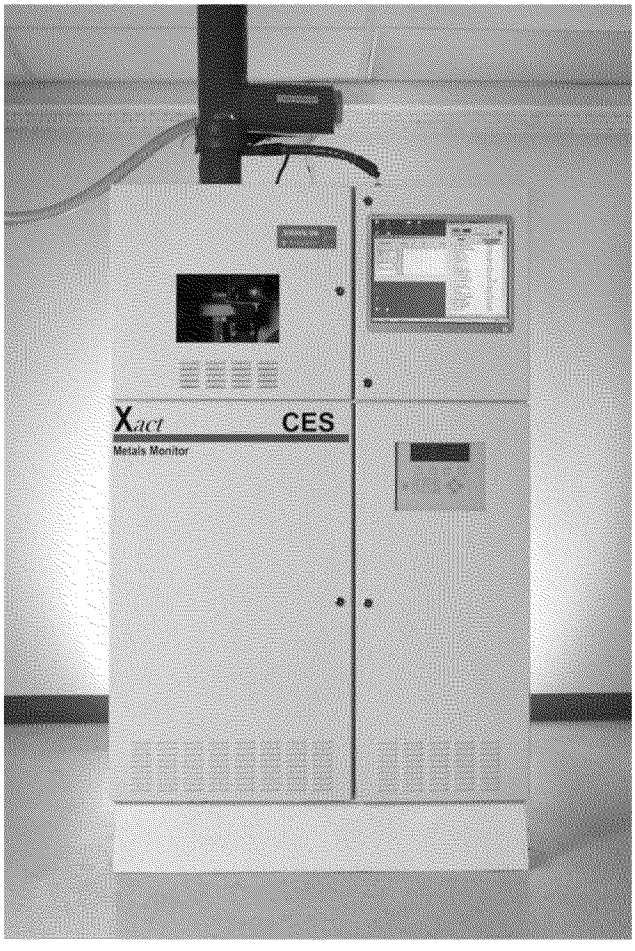

Figure 17. 2004 CES metals monitor.

R5-2014-0104710000365

6 Summary and Conclusions

A new prototype XCEM was constructed and installed at the TEAD APE-1236 incinerator. It underwent an M29 comparison test during a 4-day period in May 2001. During this test, the monitor functioned in a completely automated manner and automatically recorded the test data. The objective of the test was to meet the requirements of the proposed PS-10.

The monitor met the PS-10 sampling and response time criterion by having an effective up-time of 100 percent and reporting time averaged concentrations every 20 minutes (20-minute lag between sampling and reporting). It also met the QA criterion with a precision no more than 2 percent for zero and upscale checks, and a calibration drift of 0.5 percent. The XCEM met the PS-10 RA criterion (less than or equal to 20 percent) for three of the nine metals tested: Cd, Cr, and Ni. The RA for Pb was 22 percent. The results for Ba, Sb, Zn, and As showed systematic biases. It is believed that the monitor did not successfully measure Hg because of loss to the unheated sample line. With regard to response to change in concentration, the XCEM results had a correlation (r^2) of 0.95 or better for Ni, Sb, and Zn.

In March 2002, the XCEM was moved to a closer location, heat traced, insulated, and equipped with a shrouded probe. The combined effect of these changes was to minimize Hg and PM loss in the sample line. In April 2002, several improvements were made to the calibration procedure, and the XCEM was recalibrated. The transport system was evaluated by performing a comparison test between the XCEM, predicted concentrations based on spiking, and M17 filter sampling. No measurable loss in particulates was observed. The recalibration was evaluated using a QSIS. The resulting elemental concentrations were within their expected uncertainties for all elements except Cd and Ag.

In May 2002, a series of 12 comparison tests with EPA's M29 were conducted. During this testing, the XCEM had an "uptime" of better than 98 percent, met all QA 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.

R5-2014-0104710000365

APE-1236 emissions have the potential to approach state-mandated emission limits for three elements: Pb, Cd, and Cr. The XCEM met the PS-10 20 percent RA criterion for all three of these elements. XCEM data were 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 nonregulated element, Zn, was also spiked and examined during validation testing. The XCEM met the RA criterion for Ba and Sb, 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 Cd, Cr, and Sb, calibration appeared to cause some error, even though these elements still met the RA criterion. However, for As, Ni, and Zn, the XCEM calibration was not the primary source of error. Other potential XCEM sources of error such as loss during transport, low filter trapping efficiency, and deposit positioning errors are highly unlikely because they would result only in XCEM concentrations lower than M29. 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 6 weeks later showed a loss of 30 percent 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. It is evident that the most significant obstacle in meeting the PS-10 RA criterion for the XCEM is the accuracy problems of the comparative reference method (M29).

It was observed for both M29 comparison tests that the best method for calibrating the XCEM had not been determined. Both tests revealed some errors in calibration with some corrections made after the M29 tests but prior to the XCEM result submissions. This may cause some speculation over the performance of the monitor because the calibration rules seemed to change after the tests started. Because this monitor samples in a nondestructive manner, the results can be reanalyzed and verified at a later date. It is these analyses that allow the determination of the sources of error, including calibration. This has clearly benefited the development of the XCEM calibration procedures with each subsequent test. However, to ensure confidence in the monitor's eventual use in the

R5-2014-0104710000365

field, a reliable, consistent, and accurate calibration protocol needs to be established.

With the assistance of the XCEM, TEAD was able to identify that blocking the bypass duct on the 1236 furnace with a metal plate resulted in a greater than 90 percent drop in metal concentrations. The continued use of the XCEM to diagnose and assist with process control at TEAD indicates the value of having an installed CEM for multi-metals.

The current cost estimates for the Army to purchase and operate a new XCEM are between $243,000 and $253,000 in capital costs, and between $32,400 and $48,300 for annual costs. These figures were current in July 2004. Recently, AED and Eli Lilly purchased XCEMs for their furnaces. Improvements in the XCEM have resulted in a monitor that can measure 25 metals simultaneously and with detection limits between 0.1 and 0.2 µg/dscm. In addition, CES has recently developed the QAG spiking method that will provide a reliable, consistent, and accurate means for ensuring that the calibration has been entered correctly.

R5-2014-0104710000365

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R5-2014-0104710000365

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R5-2014-0104710000365

Appendix A: Test/QA Plan for Verification of a Continuous Emission Monitor for Multi-metals at Tooele Army Depot (2001)*

1.0 INTRODUCTION

1.1 Test Description

This test/quality assurance (QA) plan provides detailed procedures for a verification test for an X-Ray Fluorescence-based Continuous Emissions Monitor (XCEM) used to measure metals in source emissions. The U.S. Army Construction Engineering Research Laboratory (CERL) will perform the verification test. The U.S. Army is interested in identifying an effective means of continuously measuring metals in stack emissions generated by their demilitarization incinerators. The U.S. Environmental Protection Agency's (EPA's) Environmental Technology Verification (ETV) Program will verify the test procedures and results. The purpose of the ETV is to provide objective and quality assured performance data on environmental technologies, so that users, developers, regulators, and consultants have an independent and credible assessment of what they are buying and permitting.

Battelle Memorial Institute, headquartered in Columbus, Ohio, is EPA's partner for the ETV Advanced Monitoring Systems (AMS) Center. The scope of the AMS Center covers verification of monitoring methods for contaminants and natural species in air, water, and soil. Verification testing will follow procedures specified in this test/QA plan and the quality requirements in the "Quality Management Plan for the ETV Advanced Monitoring Systems Pilot" (EPA 2000).

* Prepared for CERL by Cooper Environmental Services, Beaverton, OR, 8 May 2001.

Testing will take place at the Tooele Army Depot (TEAD) deactivation furnace located in Tooele, UT.

1.2 Test Objective

The objective of the verification test is to quantify the performance of the XCEM by comparison to reference metal measurements under full-scale conditions at a combustion facility.

1.3 Organization and Responsibilities

The CERL, TEAD, and Battelle will perform and evaluate the verification test in cooperation with Cooper Environmental Services (CES), which will provide the XCEM for verification. MSE Technology Applications, Butte, MT (MSE-TA) will be responsible for spiking the stack, and the U.S. Army Center for Health Promotion and Preventive Maintenance (CHPPM) will conduct the reference method testing. The organization chart in Figure 1-1 shows the individuals who will have responsibilities in the verification test. The specific responsibilities of these individuals are detailed in the following paragraphs.

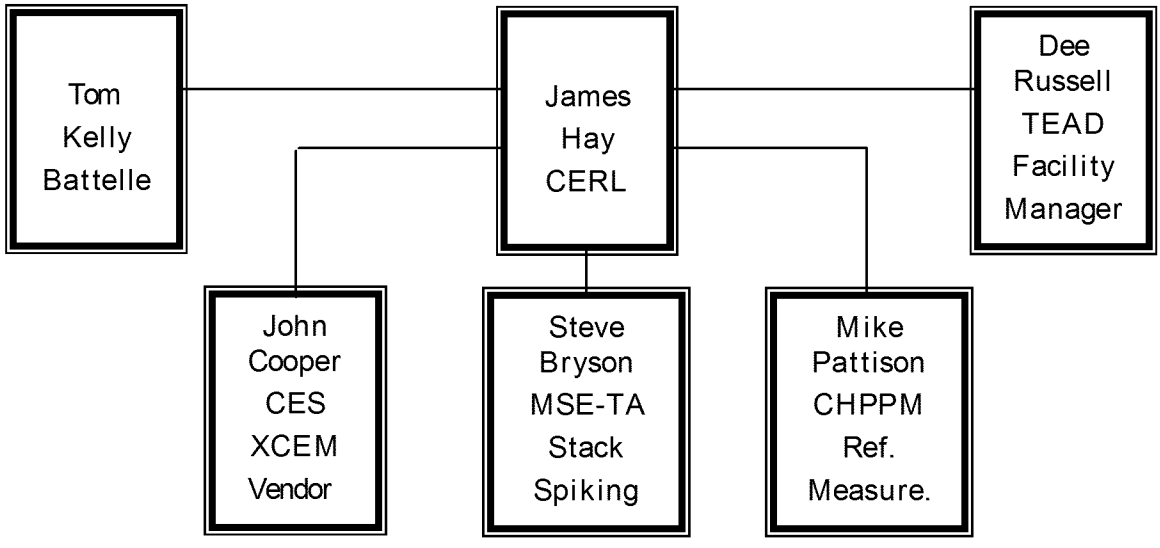

Figure 1-1. Organizational Chart for Verification Tests

1.3.1 Construction Engineering Research Laboratory

Dr. K. James Hay is the CERL verification testing leader. Dr. Hay will have overall responsibility for ensuring that the technical, schedule, and cost goals established for the verification test are met. If questions arise concerning QA

problems, Dr. Hay has the authority to stop or delay the test. As the test leader, Dr. Hay will:

- Coordinate TEAD, Battelle, CHPPM, MSE-TA and CES staff to conduct the verification test.
- Have overall responsibility for development of a test/QA plan.
- Revise the draft test/QA plan in response to reviewer's comments.
- Have overall responsibility for ensuring that this test/QA plan is followed.
- Serve as the primary point of contact for CES representatives.

1.3.2 Battelle

Dr. Thomas J. Kelly is the ETV AMS Center's Verification Testing Leader. In this role, Dr. Kelly will be responsible for reviewing the test/QA plan, evaluating field-testing to ensure that the test/QA plan is being followed, and developing an ETV verification report and statement. Mr. Charles Lawrie is the AMS Center's Quality Manager. As such, he will be responsible for assessing that quality requirements of this test/QA plan are met. More specifically, these Battelle staff will:

- Review the draft test/QA plan.
- Coordinate Battelle and EPA/ETV staff during verification testing.
- Observe the CHPPM/MSE-TA/CES team in their performance of the verification test.
- Report test quality problems to CERL. If significant quality problems are observed and not rectified, Battelle can discontinue the test as an ETV verification.
- Prepare a draft ETV verification report and statement using test data and summary test report provided by CES.
- Oversee revision of the draft ETV verification report and statement in response to reviewer's comments.
- Coordinate technical peer reviews of the test/QA plan and ETV verification report and statement.
- Conduct a technical system audit and report results of that audit.

1.3.3 Tooele Army Depot

The verification test will be conducted in collaboration with Dee Russell of TEAD. Mr. Russell's responsibilities are:

- Coordinate the operation of the facility during verification testing.
- Coordinate the installation of the XCEM at the TEAD incinerator.
- Communicate needs for safety and other training of staff working at the facility.
- Contribute to the development of the draft test/QA plan.

- Provide input on facility operating conditions and procedures for the summary and ETV verification report.
- Review the draft test/QA plan.
- Provide input for the summary test report and ETV verification report.
- Review draft reports.
- Assemble trained staff to operate the TEAD incinerator.
- Ensure that the facility is fully functional prior to the times/dates needed in the verification test.
- Oversee technical staff in facility operation during the verification test.
- Ensure that operating conditions and procedures for the TEAD incinerator are recorded during the verification test.
- Review and approve all data and records related to facility operation.
- Provide support in responding to any issues raised in assessment reports and audits related to facility operation.

1.3.4 Cooper Environmental Services

Cooper Environmental Services of Beaverton, OR manufactures the XCEM. CES staff will:

- Develop the draft test/QA plan and submit plan to CERL, Battelle, TEAD, CHPPM, and MSE-TA staff. Revise the test/QA plan in accordance with reviewers' comments.
- Approve the final test/QA plan.
- Participate in required safety training at the test facility before installation of the XCEM.
- Attend a pre-study site visit to review facility requirements for testing.
- Provide an XCEM for the duration of the verification test.
- Commit a trained technical member of staff to operate, maintain, and repair the XCEM throughout the verification test.
- Participate in verification testing, including providing data acquisition for the XCEM.
- Provide data from the XCEM at the conclusion of each test day.
- Prepare a summary test report for CERL. The summary test report will be used as the basis for the ETV verification report.
- Review the draft verification report and verification statement.

1.3.5 Center for Health Promotion and Preventive Medicine

Reference method testing will be conducted by CHPPM under the direction of Mike Pattison. Mr. Pattison will:

- Review the draft test/QA plan.
- Adhere to the quality requirements in this test/QA plan.

- Assemble trained technical staff to conduct reference method sampling for the verification test.
- Contract for and oversee laboratory analysis of the reference method samples.
- Provide reference method analytical and quality assurance results and data in an agreed-upon format to Battelle, CES, and/or CERL as needed.
- Provide support in responding to any issues raised in assessment reports and audits related to facility operation.

1.3.6 MSE Technology Applications, Inc.

MSE-TA will be responsible for injection of the metals of interest into the TEAD incinerator. MSE-TA will:

- Quantitatively spike metals of interest into the TEAD incinerator downstream of the controls.
- Provide measurable concentrations of the metals of interest at the XCEM and reference method sampling points.
- Ensure that particle size for the metals of interest are representative of typical stack gas conditions.
- Ensure that all applicable regulatory emission limits are maintained.

1.3.7 U.S. Environmental Protection Agency

EPA manages the ETV program and partners with Battelle for the ETV AMS Center. As such, EPA has the option to conduct a technical systems audit of the verification test. In addition, EPA will participate in the peer review of the test/QA plan to be prepared by CES and the ETV verification report to be prepared by Battelle.

2.0 APPLICABILITY

2.1 Subject

This test/QA plan is applicable to the verification testing of a commercially available continuous emission monitor (CEM) system for determining multi-metal concentrations in combustion source emissions. The system being tested is an X-ray Fluorescence-based CEM (XCEM) manufactured by CES. The XCEM extracts a representative stack gas sample and concentrates the particulate matter and gas phase hazardous metals on a filter, which is then analyzed with x-ray fluorescence (XRF) using an adapted QuanX analyzer. A prototype of the

R5-2014-0104710000365

XCEM was assessed at the MSE-TA test facility in Butte, MT (Bryson 2000) and has been redesigned for increased ease-of-use and automated QA routines.

Verification testing will be conducted at TEAD. The TEAD facility has a well-characterized feedstream and was the site for multi-metal CEM tests conducted in 1999.

The TEAD site has a deactivation furnace, APE-1236, for incineration of munitions. The incinerator is currently regulated under the Resource Conservation and Recovery Act (RCRA) for antimony, arsenic, barium, beryllium, cadminum, chromium, lead, mercury, nickel, selenium, silver, and thallium (Sb, As, Ba, Be, Cd, Cr, Pb, Hg, Ni, Se, Ag, and Tl). Of the twelve regulated elements, five are typically found in the feedstream: Sb, Ba, Cd, Cr, and Pb. The XCEM will be verified for its measurement capabilities of the five elements found in the feedstream as well as As, Hg, Ni and a nonregulated metal, zinc (Zn). These elements were selected in order to challenge the XCEM over a large range of analysis conditions and elemental concentrations.

EPA Method 29 (M29) is currently recognized as the most suitable procedure to determine multi-metal concentrations in source emissions (EPA 1990). Method 29 draws stack gas through a filter and a series of impingers providing a 1- to 3-hour average concentration. For the verification testing, a battery of twelve 2-hour M29 tests will be conducted by CHPPM. Analysis of the M29 sample train will be under the direction of CHPPM and will include, as a minimum, determination of the nine elements measured by the XCEM.

2.2 Scope

The overall objective of the verification test described in this plan is to provide quantitative verification of the performance of the XCEM under real-world conditions. EPA has published a draft performance specification document designated as PS-10 (EPA 1996) as a proposed description of how to assess the acceptability of a multi-metal CEM upon installation and thereafter. The goals of the verification test will be met if the XCEM meets the proposed PS-10:

1. *Relative accuracy criteria* for the elements in the feedstream of the Tooele incinerator (Sb, Ba, Cd, Cr, and Pb).
2. *Quality assurance criteria* by passing daily zero, span, and drift checks.
3. *Response time and reporting time criteria* for a batch CEM.
4. *Measurement criteria* by testing several elements at two concentration levels (Hg, Ni, Zn, and Sb).

R5-2014-0104710000365

A secondary objective is to meet the relative accuracy criteria for additional regulated and unregulated metals, which are not typically found in the feedstream (As, Hg, Ni, and Zn).

The performance parameters that are addressed by this test/QA plan include:

- Relative accuracy
- Correlation with reference method
- Precision
- Instrument drift
- Span and zero
- Response time
- Bias
- Low level metal response.

Relative accuracy, correlation with the reference method, and precision (i.e., repeatability at stable test conditions) will be assessed for the elements being measured by the XCEM. Instrument drift will be based upon the precision of the daily XCEM span and zero QA measurements. The XCEM has a built-in additional check for instrument drift which measures a palladium standard with each XCEM test run. For the verification test, response time will be determined as the time between the start of one sampling period and the beginning of a second sampling period. Bias will be identified using EPA method 301 protocols as discussed in section 5.6. Low-level metal response will be determined by a comparison to chromium and arsenic reference method concentrations, which will be less than 6 and 18 µg/dscm respectively.

It is beyond the scope of this verification test to simulate the aging and exposures that may affect an XCEM during routine long-term use. This verification test evaluates the performance of a new XCEM over a relatively short test period, in the hands of staff skilled in its operation. It must be noted that the long-term performance may be different from that observed in the testing described here. The effort spent in installing and maintaining the XCEM will be documented, however, and the amount of time the XCEM is operational over the verification test period will be recorded, to assess data completeness.

3.0 SITE DESCRIPTION

Verification testing will take place at the TEAD building 1320 deactivation incinerator APE-1236 (Figure 3-1). This section of the test/QA plan describes the TEAD incinerator and the procedures for operating it for this test.

3.1 Test Facility

The TEAD incinerator, which runs on diesel fuel, is designed to incinerate decommissioned munitions. Typical operating parameters for the incinerator are shown in Table 3-1. The TEAD incinerator is classified as a dry stack with water content ranging from 5 to 10 percent. Typical stack PM concentrations are in the 10 mg/dscm range. A number of sensors (temperature, gas flow, pressure differential, combustion gases, etc.) are used to monitor operating conditions at various points in the system. Signals from these sensors are monitored and compared to preset operating standards. The incinerator consists of a main control panel, CEMS, Waste Feed Rate Monitoring System (WFRMS), dual conveyor feed system, rotary furnace, furnace shroud, cyclone, afterburner, discharge conveyor, high temperature cast ceramic filters baghouse, high temperature draft fan, and exhaust stack.

1) Main Control Panel. The main control panel contains various pieces of control equipment to monitor and control the furnace operation. Process controllers are used to control the rotary furnace feed end temperature, negative pressure in the furnace, and afterburner temperature. A multi-point digital recorder is used to record process parameters. Logic control for the furnace is performed by a PLC. The PLC controls the motor starters, the WFRMS, safety interlocks, and alarms. The computer system is an industrial-based machine running data acquisition software, which provides centralized and integrated data management, process graphics, operator interface, and report generation.

Figure 3-1. TEAD Deactivation Incinerator Building 1320.

Table 3-1. Typical operating parameters for the APE-1236 deactivation furnace.

Typical Operating Parameters for the APE-1236 Deactivation Furnace	
Afterburner Temp. (°F)	1600
Baghouse ΔP (in. H_2O)	9
Baghouse Temp (°F)	680
Kiln Feed End Draft Pressure (in. H_2O)	0.3
Kiln Feed End Temp (°F)	600
Kiln Burner End Temp (°F)	1200
O_2 – CEM (%)	14
CO (ppm)	11
Stack Temp. (°F)	550
Stack Gas Velocity (ft/sec)	46
Stack Pressure (in. H_2O)	0.3

Figure 3-2. TEAD Incinerator Stack.

2) Continuous Emissions Monitoring Systems. CEM systems are in place to measure carbon monoxide (CO) and oxygen (O_2) in the exhaust stack. The CEM sampling system includes the following: sample extraction probe, heat traced sampling lines, calibration ports, refrigerated condenser, sample pump, filters, and flow meters. The sample extraction port is located in the exhaust stack approximately 20 feet above grade. The CEM system includes automatic calibration, which allows the monitors to be calibrated periodically without operator intervention. The CO monitor is a NDIR analyzer with 0-200 ppm and 0-3,000 ppm dual range capability. The output from the CO monitor is corrected to 7 percent O_2 (using data from the O_2 CEM).

3) Waste Feed Rate Monitoring System. The WFRMS controls the furnace feed rate. The WFRMS consists of a precision explosion proof scale, a push-off box, and a slide chute. The scale reports the measured weight to the PLC via a serial communication cable. The PLC verifies that the weight is less than or equal to the established limit for the item being incinerated. Once the PLC has verified that the weight is acceptable, the push-off box pushes the ammunition item onto the slide chute, which is over the primary feed conveyor. The WFRMS is capable of cycling every 15 seconds.

4) Dual Conveyor Feed System. The primary waste feed conveyor transports the munitions from the WFRMS through the concrete wall into the barricade area. The ammunition is then fed onto the secondary feed conveyor, which deposits the ammunition into the rotary furnace feed chute. If an out-of-parameter condition arises, the primary feed conveyor is stopped until the condition is corrected. For safety reasons, however, the secondary conveyor continues to operate. This allows munitions near the high temperature end of the kiln to continue moving through the furnace and deters possible explosions outside the furnace.

5) Rotary Furnace. The rotary furnace is designed to ignite the ammunition items and effectively incinerate reactive components from the metal shells. The heat to ignite the ammunition is initially provided by fuel oil forming a counter-current to the movement of the ammunition through the rotary furnace. Combustion gases and entrained ash exit the furnace adjacent to the feed chute. Non-entrained ash and the metal components of the ammunition are discharged at the burner end of the rotary furnace. The ammunition is propelled through the 20 ft long, 30.5 inch diameter retort toward the burner end by spiral flights. As the ammunition approaches the flame, they either detonate or burn freely, depending on the ammunition characteristics. The thick cast steel walls contain high order detonations. Feed rates, residence times, and operating parameters have been established for each ammunition item by controlled testing. The ro-

R5-2014-0104710000365

tary furnace is equipped with a Hauck 783 proportioning burner located at the discharge end. The burner has a capacity of 3 million BTU/hr and a nominal turndown ratio of 4:1. The feed end temperature of the furnace ranges between 350-450 °F while the discharge end ranges from 800-1100 °F during normal operation. The rotary furnace is operated under a slight negative pressure.

6) Furnace Shroud. A metal shroud that completely encloses the retort sections, the draft fan, and the retort combustion air fan controls fugitive emissions from the rotary furnace. The draft fan is used to maintain negative pressure at the feed end of the furnace. The retort combustion air fan draws air from the area beneath the retort shroud, creating a negative pressure. The combustion air blower creates a negative pressure inside the shroud, which pulls any fugitive emissions through the blower and discharges them into the furnace via the furnace burner.

7) Cyclone. Large particles from the gas stream are removed by the cyclone. The cyclone has a 90-95 percent removal efficiency for particles 10 microns and larger. The cyclone has a clock-wise rotation, with inlet and outlet ducts at 90° separation. Particles are removed from the cyclone at the bottom by a double tipping valve. The valve has two gates that are motor driven. The gates open alternatively so that only one gate is open at any time, thus maintaining the negative pressure.

8) Afterburner. The afterburner is built to AED specifications by Southern Technology Incorporated. The afterburner is designed to raise the temperature of the exhaust gases exiting from the kiln. This elevated temperature, and the added residence time, enhances the complete combustion of the explosive. The afterburner is capable of heating 4000 scfm of flue gas from 350-450 °F to 1400-1600 °F with a minimum flue gas residence time of 2 seconds. A diesel fuel burner with a propane pilot ignition system heats the afterburner. The afterburner is equipped with a Hauck WR0164 wide range burner with a capacity of 8 million BTU/hr and nominal turndown ratio of 10:1.

9) Discharge Conveyor. The solid waste exits the furnace by the discharge conveyor located at the discharge/burner end. The solid waste is typically comprised of the metal casings, melted lead projectiles, and residual ash. The low end of the discharge conveyor is located underneath the discharge/burner end of the rotary furnace. The high end of the conveyor passes through the concrete barricade wall and deposits the waste into containers.

10) High Temperature Cast Ceramic Filters Baghouse. The baghouse is a high temperature cast ceramic collector, used for final particulate cleansing for

the gas stream. The baghouse was designed and built to AED specifications by JT Systems Incorporated. The flue gases from the afterburner are transported to the baghouse by 120 ft of 30-inch diameter stainless steel ducting. The ducting is long enough to produce a temperature drop from 1600 °F at the exit of the afterburner to 1000 °F entering the baghouse. The baghouse contains 154 cerafil ceramic candles that are 5.75 inches in diameter and 10 ft long. This results in a total filter area of 2330 square feet with a filtration velocity of 4.97 feet/second. The baghouse operates with a delta pressure range of 0.5 to 6.0 inches of water column. The particles settle into the hopper below and are exhausted through a double tipping gate valve into a sealed 55-gallon drum while maintaining an air seal on the baghouse assembly.

11) High Temperature Draft Fan. The gas steam is pulled though the APCS by an induced draft fan. The fan is a Fan Equipment Company Model M-21 I.E. The fan is capable of pulling 6700 ACFM at a draft (negative pressure) of 30 inches of water column.

12) Exhaust Stack. The A36 carbon steel, circular exhaust stack is approximately 30 ft high (34 ft with extension) and has a nominal ID of 20 inches (Figure 3-2).

3.2 TEAD Emission Limits During Testing

For the verification test, metals in the TEAD incinerator stack gas are regulated under a Temporary Authorization permit as shown in Table 3-2. Of the 12 regulated metals, 5 are typically found in the feedstream (Pb, Sb, Ba, Cd, and Cr); however, Pb is the only element that is routinely found in measurable concentrations in the stack gas.

Table 3-2. TEAD metal emission limits during verification testing.

Element	Limit (g/hr)	Element	Limit (g/hr)
Antimony (Sb)	14	Lead (Pb)	4.3
Arsenic (As)	0.11	Mercury (Hg)	14
Barium (Ba)	2400	Nickel (Ni)	930
Beryllium (Be)	0.20	Selenium (Se)	180
Cadmium (Cd)	0.26	Silver (Ag)	140
Chromium (Cr)	0.04	Thallium (Tl)	14

4.0 EXPERIMENTAL DESIGN

4.1 General Design

For all tests, both the kiln and the afterburner will be fired with diesel fuel while incinerating Mark 344 fuses (NSN number 1325000090348) with a feed rate of 79 per hour. The chemical composition of the fuses is shown in Table 4-1. For these fuses, lead is the restrictive element limiting the feed rate. Table 4-2 shows the nine elements that will be measured by the XCEM during verification testing. Eight of these metals will be spiked directly into the stack downstream of the controls. These metals will be spiked at the level shown in Table 4-2. Lead, however, will not be spiked since the incinerated munitions provide measurable concentrations of lead without spiking.

Spiking will be conducted by MSE-TA using three or four atomizers to inject solutions containing the metals of interest either directly into the stack or into a chamber that dries the solution prior to entering the stack. The atomizer provides liquid droplets that, when dried, yield fine salt particles that are representative of typical stack aerodynamic diameters.

Stack gas metal concentrations will be simultaneously determined by the XCEM and two Method 29 (M29) sampling trains. The M29 trains will sample for two hours while XCEM data, which is recorded every 20 minutes, will be averaged for the M29 test run.

A total of 12 dual M29 test runs will be performed by CHPPM. Each run will include two M29 sampling trains in order to determine reference method precision. Method 301 will be applied to M29 data to determine bias between the reference method sampling trains. Prior to testing, CHPPM will conduct an EPA Method 2 velocity traverse to determine a representative sampling point for the M29 probes. The XCEM and M29 probes will be located approximately 27 feet above the base of the exhaust stack. The nearest flow disturbances are located 9.8 duct diameters upstream (induced draft fan) and 4.3 duct diameters downstream (top of the stack) from the sample ports.

Table 4-1. Composition of munitions incinerated during metals testing.

Fuze, Bomb, Tail, MK344 Mod 0/1 Feed Rate: 79 items/hr; Loading (lb/item) 0.2791		
Component	**Component Quantity (lb/item)**	**Component Feed Rate (lb/hr)**
Butyl Acetate	0.00001	0.0008
Charcoal	0.00002	0.0016
Ethyl Alcohol	0.00001	0.0008
Graphite	0.00541	0.4275
Lead Azide	0.00028	0.0221
Lead Monoxide	0.00005	0.0040
Lead Powder	0.00031	0.0245
Lead Styphnate	0.00683	0.5398
Nitrocellulose	0.00002	0.0016
Nitrostarch	0.00001	0.0009
PETN	0.00031	0.0245
Potassium Nitrate	0.00008	0.0063
Selenium Powder	0.00012	0.0095
Sulfur	0.00005	0.0040
Tetryl	0.26555	20.9855
Toluene	0.00001	0.0008

Table 4-2. Tooele metal emission limitations and spiking levels.

Elements	Emission Limits[1]		Spiking Level[1]	
	g/hr	~ µg/ dscm	~ µg/ dscm	
			Runs 1-6	Runs 7-12
As	0.11	17	15	15
Ba	2,400	360,000	1000	1000
Cd	0.26	39	35	35
Cr	0.04	6.5	5.5	5.5
Hg	14	2,100	100	300
Ni	930	139,500	200	500
Pb	4.3	645	NS	NS
Sb	14	2,100	200	500
Zn	NR	NR	200	500

1 The concentration in µg/dscm assumes a stack flow rate of about 6700 dscm/hr
NR: Not regulated NS: Not Spiked

R5-2014-0104710000365

CHPPM will conduct the chemical analysis of recovered sample fractions from the M29 trains. Sample handling, analysis, and all associated QA/QC activities will conform to the requirements of M29. Accuracy data for metals analysis will be confirmed with two field spikes of the nine measured metals into blank sampling trains. Media blanks of the M29 solutions and filter will also be analyzed. Sample integrity will be maintained by use of a chain-of-custody and a designated sample custodian. Unique sample identification numbers will be implemented so that final data used for verification can be traced back through the analytical process to the original sample.

4.2 Test Schedule

Set-up for the verification testing is scheduled for May 10. XCEM verification testing is tentatively scheduled for May 11, 12, 14, and 15. Three M29 test runs are planned for each day with each run lasting 2 hours. All nine metals of interest will be tested during each run; however, lower concentrations of Ni, Sb, Hg, and Zn are scheduled for the first six runs as shown in Table 4-2.

4.3 Test Procedures

In all cases when reference method data is being taken, the introduction of the indicated metals will be held constant throughout the entire sampling period. The intent of this approach is to allow comparisons of XCEM data to reference method data under constant conditions.

4.3.1 Spiking approach

Spiking will be conducted by MSE-TA of Butte, MT. Three atomizers are used to quantitatively inject nitric acid solutions containing the metals of interest. The solution will be injected either directly into the stack or into a drying chamber, which opens to the stack. The spiked solution will enter the stack through a port located at the base of the stack. This port was successfully used in earlier multi-metal CEM tests at Tooele and is directly downstream of a draft fan allowing for good mixing.

Manufacturer specifications for the atomizers determine droplet size distributions based on pressure and air flow rate. For these tests, pressure and flow rate will be maintained to keep droplet sizes less than 28 microns in diameter. When dried, the majority of the mass is expected to be in the one to four micron range.

Each atomizer has been gravimetrically calibrated by MSE-TA to determine mass emission rates over the range of pressure and air flow rates expected for the verification test.

4.3.2 Reference method sampling

CHPPM's Air Quality Surveillance Program will conduct reference method sampling. Dual sample trains will be used to collect metals data employing standard operating procedures from M29. Full sample custody procedures will be employed during the test using sample custody sheets and sample custody seals. Samples will be under either direct custody or lock and key at all times. Per M29 protocol, media blanks from the same lot as used during testing will be taken and treated in the same manner as the test run samples.

Dry gas meters are calibrated both pre- and post-tests with a wet test meter. Pitot tubes undergo a geometric calibration, and thermocouples are calibrated using standard two point calibration methods.

As a performance audit, two blank trains will be quantitatively spiked with all nine of the metals of interest. These spikes will be conducted on sampling media, including the filter and impinger solutions, from the same lots used during testing. A spike recovery target of 80 to 120 percent of injected solution has been set.

4.3.3 Reference method analysis

Reference method analyses will be conducted by CHPPM's Directorate of Laboratory Services (DLS). Analysis will follow standard M29 protocol with the following exception: the front half analysis will include separate reported values for both the front half rinse and the filter. Blank values will be determined using M29 section 9.1 protocols and a standard blank subtraction will be made if significant metals are found in the blank.

CHPPM uses ICP-MS for its metals analysis. The ICP-MS is calibrated using solution standards as discussed in section 10.2 of M29.

4.4 Data Comparisons

This section describes how the reference and CEM data will be used and compared to quantify the performance of the XCEM. Table 4-5 summarizes the data that will be used for the verification comparisons.

Relative accuracy and correlation will be determined by comparing the CEM results against the M29 results, for each metal. M29 results for the probe, front half, and back half will be reported separately to evaluate potential particle loss in the XCEM tubing. However, the total train results will be combined for the relative accuracy and correlation calculations.

Precision will be determined by analysis of XCEM concentrations when the spike injection rate and stack conditions are held constant. It is recognized that the reported precision will include variability in stack conditions as well as XCEM variability.

Table 4-5. Summary of data to be obtained during XCEM verification test.

Performance Parameter	Objective	Comparison Based On	No. of Data Points
Accuracy	Determine degree of quantitative agreement with reference method.	Reference Method Results	12
Correlation	Determine degree of correlation with reference method.	Reference Method Results	12
Precision	Determine degree of consistency in XCEM measured concentrations under constant operating conditions.	XCEM reported concentrations under constant operating conditions.	6/run
Instrument Drift	Determine XCEM ability to measure consistently over the course of the test.	Determine variation in palladium concentrations determined with each XCEM measurement	3/hr
Span and Zero	Determine XCEM response under maximum and minimum conditions	XCEM automated daily QA routine	4
Response Time	Determine XCEM response time as a batch CEM.	Continuous monitoring of metal concentrations	3/hr
Bias	Determine if bias exists between M29 and the XCEM.	Reference Method Results	12
Low Level Metal Response	Determine XCEM performance when low metal concentrations are present in the stack.	Arsenic and chromium ref. Method results	24

Instrument drift will be determined by evaluation of XCEM reported palladium concentrations. As part of the XCEM quality assurance program, a palladium rod has been permanently fixed above the x-ray beam and below the filter tape. The palladium rod is measured with each sample, and a running record of the reported concentrations is maintained. The percent relative standard deviation for palladium concentrations will also serve as a determination of XCEM instrument drift during testing.

XCEM response time will be determined as the time between the start of one sampling period and the beginning of a second sampling period. The XCEM samples for 10 to 20 minutes, depending upon the desired detection limits. Within a few seconds of sampling, the exposed tape is moved into the XRF analysis region. Analysis requires the same amount of time as sampling. Following analysis, concentrations are determined and recorded in a fraction of a second. For these tests, the response time will be determined as the average time from the start of one sampling period to the start of the next sampling period with a delay in the reporting of data that is equivalent to the analysis time.

Bias between the dual M29 sampling trains for each run will be determined by a comparison of the dual M29 sample runs using an EPA Method 301 approach for paired sampling trains. For valid test runs, M29 concentrations will be averaged and compared to reported XCEM data.

The XCEM's ability to measure low-level concentrations of metals will be challenged by Cr, As, and Cd, which are to be present at approximately 5, 15, and 35 µg/dscm respectively.

M29 results identified as outliers will be reported, but will not be used for verification. The intent of this approach is to provide a valid set of reference data for verification purposes, while also illustrating the degree of variability of the reference method. Identification of outliers will be based upon analysis of percent differences in M29 concentrations between sampling trains and trends in data throughout the test day. In any case, where rejection of a reference result is suggested, effort will be made to find an assignable cause for the divergent result.

According to PS-10, the XCEM acts as a batch CEM. Batch CEMs continuously sample and concentrate the pollutant on a capture medium. Analysis is performed after sufficient time has elapsed to concentrate the pollutant to levels that are detectable by the analyzer. PS-10 requires that batch CEMS meet three response time criteria:

1. The sampling time shall be no longer than one-third of the averaging period for the applicable standard.

2. The delay between the end of the sampling period and reporting of the analysis period shall be no greater than 1 hour.
3. Sampling shall be continuous except in that the pause in sampling when the sample collection media is changed should be no greater than 5 percent of the averaging period or 5 minutes, whichever is less.

TEAD incinerator emissions are regulated by two standards: Resource Conservation and Recovery Act (RCRA) limits in grams per hour and the maximum achievable control technology (MACT) rule, which regulates using a 12-hour rolling average. Since the RCRA limits are more stringent, the response time shall be limited to 20 minutes for the TEAD tests with sampling occurring at least 57 minutes per hour.

Span and zero determinations will be conducted daily by the XCEM. The automated XCEM span routine extends a plunger containing metals of interest into the analysis area. The plunger is then analyzed by the XCEM and the data compared with the known metal concentrations on the plunger. Zero readings are determined by analysis of blank filter tape.

The XCEM filter analysis is nondestructive and the exposed tape remains available for subsequent analysis. In cases where unexplained discrepancies exist between XCEM and M29 data, a post-test filter tape analysis will be considered.

Setup and maintenance needs will be documented qualitatively by Battelle, both through observation and through communication with the vendors during the test. Factors to be noted include the frequency of scheduled maintenance activities, the downtime of the CEM, and the number of staff operating or maintaining it during the verification test.

5.0 STATISTICAL CALCULATIONS

Statistical calculations will be used to verify the performance of the XCEM as described below. In all cases, measurement results from both the reference method and the XCEM are reported in units of $\mu g/m^3$ on a dry basis at 20 °C, 1 atmosphere pressure, and the actual flue gas O_2 content.

5.1 XCEM Concentrations During a Reference Method Run

Average XCEM concentrations for a given reference method run will be calculated as follows:

$$C_i = \frac{\sum_{j=1}^{n} C_{ij} t_j}{\sum t_j} \qquad \text{[Eq 5.1]}$$

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*

5.2 Relative Accuracy

The relative accuracy (RA) of the XCEM with respect to the reference method (M29) will be assessed by:

$$RA = \frac{\left|\bar{d}\right| + t_{n-1}^{\alpha} \frac{S_d}{\sqrt{n}}}{\bar{x}} x100\% \qquad \text{[Eq 5.2]}$$

Where *d* refers to the difference between M29 and the XCEM results, and *x* corresponds to the M29 result. S_d denotes the sample standard deviation of the differences, while t^{α}_{n-1} is the t value for the $100(1-\alpha)^{th}$ percentile of the distribution with n^{-1} degrees of freedom. The RA will be determined for an α value of 0.025 (i.e., 97.5 percent confidence level, one-tailed). The RA calculated in this way can be interpreted as an upper confidence bound for the relative bias of the analyzer, i.e., $\frac{\left|\bar{d}\right|}{\bar{x}}$, where the superscript bar indicates the average absolute value of the differences of the reference values. If 12 reference method test runs are completed, the RA procedure stated in PS-10 will be followed (i.e., up to three results may be omitted from the RA calculation). The impact of the number of data points (n) on the RA value will be noted in the verification report. The RA will be calculated separately for each metal measured by the XCEM.

5.3 Correlation with Reference Method

The degree of correlation of the XCEM with the reference method results will be assessed in terms of the correlation coefficient (r^2) for metals spiked at more than one concentration (i.e., Hg, Ni, Zn, and Sb).

A second series of intra-method correlations will be determined by comparing the relative ratios of metals measured by the XCEM for each of the measurement periods. This correlation assumes that no fractionation of the injected species occurred during transport.

5.4 Precision

Precision will be calculated in terms of the percent relative standard deviation (RSD) of a series of XCEM measurements made during stable operation of the TEAD, with metals injected at a constant level. This precision will reflect the variability in the stack conditions, spiking rate, and XCEM measurements and will be identified as a maximum XCEM precision with a note in the verification report that the calculated precision is subject to the variability of the test, not only the XCEM variability. During each M29 sampling run, all readings from the XCEM will be recorded and the mean and standard deviation of those recordings will be calculated. Percent precision (P) will then be determined as:

$$P = \frac{SD}{\overline{X}} x100 \qquad \text{[Eq 5.3]}$$

where SD is the standard deviation of the XCEM readings and $\overline{X}$ is the mean of the readings. The same calculation will be performed for each metal measured by the XCEM.

5.5 Span, Zero, and Instrument Drift

The XCEM has automated daily span and zero checks and reports a palladium concentration with each sample to check for instrument drift. Span, zero, and instrument drift will be reported in terms of the mean, RSD, and range (maximum and minimum) of the readings obtained from the XCEM. The percent RSD will be calculated as:

$$RSD = \frac{SD}{\overline{X}} x100 \qquad \text{[Eq 5.4]}$$

where $\overline{X}$ is the mean, and SD is the standard deviation of the daily readings of the standard. This calculation, along with the range of data, will indicate the day-to-day variation in zero and standard readings.

5.6 Method 29 and XCEM Bias

Bias between the two M29 sampling trains and the M29/XCEM data will be determined using an EPA Method 301 approach. The results are tested for statistically significant bias by calculating the t-statistic and determining if the mean of the differences between the two sampling trains is significant at the 80-percent confidence level. The t-statistic is calculated by finding the SD of the differences between the two sampling trains.

$$SD_d = \sqrt{\frac{\sum (d_i - d_m)^2}{(n-1)}} \qquad \textbf{[Eq 5.5]}$$

Where:

d_i = the difference between the two sample train values
d_m = mean of the d_i values
n = number of paired samples

Using the SD determined in equation 5.5, the t-statistic is then calculated as follows:

$$t = \frac{d_m}{\left(\frac{SD_d}{\sqrt{n}}\right)} \qquad \textbf{[Eq 5.6]}$$

The critical value of the t-statistic is 0.8755 for 12 runs. If the calculated t-value is greater than the critical value, the bias as defined by M301 is statistically significant. A statistically significant bias in the reference method will be noted in the validation report.

Method 29 data pairs that are determined to be unbiased relative to each other will be averaged and used for comparison to the XCEM. Bias between the XCEM and average M29 data will be determined using equations 5.5 and 5.6 with d_i being the difference between the average M29 and XCEM data.

R5-2014-0104710000365

6.0 MATERIALS AND EQUIPMENT

6.1 Gases and Chemicals

6.1.1 Compressed gas

The XCEM requires about 10 scfm of dry compressed gas to provide a vacuum in the extraction system. A small amount of purified compressed gas is also used to drive the XCEM pneumatics. The atomizers used for spiking will require about 10 scfm of dry air.

6.1.2 Spike injection solutions

The spike injection solutions include $Ba(NO_3)2$, $Cd(NO_3)2$, $Cr(NO_3)3$, As_2O_3, $Hg(NO_3)2$, $Ni(NO_3)2$, $Zn(NO_3)2$, and $SbCl_2$. Solutions will be prepared on-site to allow for flexibility in responding to background metal concentrations found in the TEAD incinerator.

6.2 Reference Method

6.2.1 Sampling trains

CHPPM will supply the glassware, filters, and associated equipment for M29 sampling. Multiple trains will be supplied so that six trains (i.e., three sampling runs with two trains each) may be sampled in a single day; in addition, at least two M29 field spikes and a media blank will be analyzed. Preparation, sampling, sample recovery, and cleaning of used trains will be the responsibility of CHPPM during this verification test.

6.2.2 Analysis equipment

CHPPM will provide laboratory equipment for sample recovery and analysis. This will include all chemicals and solutions for rinsing train components and recovering impinger samples.

6.3 TEAD Monitoring Equipment

The verification will make use of monitoring equipment already integrated into the TEAD facility. This equipment includes monitors for major flue gas constituents (O_2, CO_2), as well as sensors for temperature and pressure. These devices are considered part of the TEAD facility for purposes of this test, and will be operated during this verification according to normal TEAD procedures.

7.0 QUALITY ASSURANCE/QUALITY CONTROL

7.1 Assessments and Audits

7.1.1 Technical systems audits

Battelle's Quality Manager, will perform a technical systems audit (TSA) once during the performance of this verification test. The purpose of the TSA is to ensure that the verification test is being performed in accordance with this test/QA plan, and that all QA/QC procedures are being implemented. In this audit, the reference sampling and analysis methods used may be reviewed; the actual test procedures compared to those specified in this plan; and data acquisition and handling procedures reviewed. The Quality Manager will also prepare a TSA report, the findings of which must be addressed either by modifications of test procedures or by documentation in the test records and report.

At EPA's discretion, EPA QA staff may also conduct an independent on-site TSA during the verification test. The TSA findings will be communicated to testing staff at the time of the audit, and documented in a TSA report.

7.1.2 Data quality audit

Battelle's Quality Manager will audit at least 10 percent of the verification data acquired in the verification test. The Quality Manager will trace the data from initial acquisition, through reduction and statistical comparisons, and to final reporting. All calculations performed on the data undergoing audit will be checked.

7.1.3 Assessment reports

Each assessment and audit will be documented in accordance with section 2.9.7 of the QMP for the AMS pilot. Assessment reports will include the following:

- Identification of any adverse findings or potential problems
- Space for response to adverse findings or potential problems
- Possible recommendations for resolving problems
- Citation of any noteworthy practices that may be of use to others
- Confirmation that solutions have been implemented and are effective.

7.1.4 Corrective Action

The Battelle Quality Manager, during the course of any assessment or audit, will notify the technical staff performing experimental activities of any immediate

corrective action that should be taken. Once the assessment report has been prepared, the Verification Testing Leader will ensure that a response is provided for each adverse finding or potential problem, and will implement any necessary follow-up corrective action. The Quality Manager will ensure that follow-up corrective action has been taken.

8.0 DATA ANALYSIS AND REPORTING

8.1 Data Acquisition

Data acquisition in this verification test includes recording of the response data from the XCEM, documentation of sampling conditions and analytical results from the reference method, and recording of operational data such as combustion source conditions, test temperatures, the times of test activities, etc.

Cooper Environmental Services will perform data acquisition for the XCEM during the test. For all tests, CES will be responsible for reporting the response of the XCEM to the sample provided. The XCEM data must include the results of all tests conducted each test day and are to be provided to the test manager at the end of each day. The XCEM data must include all individual readings of the XCEM (i.e., temperature, pressure, metal concentrations, QA data, etc.) listed by time of day. Averaged results over the period of an M29 sampling run will be determined following the test and provided to the test manager prior to release of M29 data.

Other data will be recorded in laboratory record books maintained by TEAD, CHPPM, Battelle, MSE-TA, and CES staff involved in the testing. These records will be reviewed to identify and resolve any inconsistencies. All written records must be in ink. Any corrections to notebook entries, or changes in recorded data, must be made with a single line through the original entry. The correction is then to be entered, initialed, and dated by the person making the correction.

In all cases, strict confidentiality of data from the XCEM will be maintained.

Table 8-1 summarizes the types of data to be recorded; how, how often, and by whom the recording is made; and the disposition or subsequent processing of the data. The general approach is to record all test information immediately and in a consistent format throughout all tests. Data recorded by CES is to be turned over to the CERL designated test manager immediately upon completion of each test day.

Table 8-1. Summary of data recording process for the verification test.

Data To Be Recorded	Responsible Party	Where Recorded	How Often Recorded	Disposition of Data
Dates, times of test events	CERL	Laboratory record books	Start/end of test, and at each change of a test parameter.	Used to organize/check test results; manually incorporated in data spreadsheets as necessary.
Test parameters (temperature, analyte identities and concentrations, flows, etc.)	TEAD, CERL, CHPPM	Laboratory record books	When set or changed, or as needed to document stability.	Used to organize/check test results; incorporated in data spreadsheets as necessary.
XCEM readings including digital displays, printouts, and electronic output.	CES	Laboratory record books, data sheets, or data acquisition system, as appropriate.	XCEM data will be recorded continuously throughout test. Data sheets will be completed as required for each test.	Electronically transferred to spreadsheets.
Reference method sampling data.	CHPPM	Laboratory record books	At least at start/end of ref. test, and at change of a test parameter.	Used to organize/check test results; incorporated in data spreadsheets as necessary.
Reference method sample analysis, chain of custody, and results.	CHPPM	Laboratory record books, data sheets, or data acquisition system, as appropriate.	Throughout sample handling and analysis period.	Transferred to spreadsheets.

8.2 Data Review

Records generated in the verification test will receive a one-over-one review within 2 weeks after generation. These reviews are to be performed within the organization generating the data. These records will then be used to calculate, evaluate, and report verification results. These records may include laboratory record books; operating data from the combustion source; XCEM data; or reference method analytical results. The review will be documented by the person performing the review by adding his/her initials and date to a hard copy of the record being reviewed. This hard copy will then be returned to the staff who

generated or who will be storing the record. Battelle will receive a copy of all written and recorded data in the project record books and a copy of the XCEM data.

8.3 Reporting

Cooper Environmental Services will prepare a summary test report for CERL documenting the testing results. The summary report will include a discussion of the XCEM performance, testing processes, and a comparison with M29 results. CES will provide Battelle with this summary test report and copies of all original raw field and laboratory data.

Battelle will prepare an ETV verification report and statement for the testing that includes the test data and a statistical evaluation of the data as described in sections 4 and 5. The verification report will briefly describe the ETV program and the AMS Center, and will describe the procedures used in verification testing. The results of the verification test will be stated quantitatively, without comment on the acceptability of the XCEM's performance. The summary test report prepared by CES will serve as the basis for the draft ETV verification report. The ETV verification report and statement will undergo a technical peer review. Final approval and distribution of the ETV verification report and statement will be conducted as stated in the Generic Verification Protocol for the Advanced Monitoring Systems Pilot.

9.0 HEALTH AND SAFETY

The verification test described in this test/QA plan will be performed at the TEAD facility in Tooele, Utah. All participants in this verification test will adhere to the health and safety requirements of the facility. Vendor staff will be operating their equipment only during the verification test. They are not responsible for, nor permitted to, operate the combustion source or perform any other verification activities identified in this test/QA plan. Operation of the XCEM does not pose any known chemical, fire, mechanical, electrical, noise, or other potential hazard.

All visiting staff at the TEAD will be given a site-specific safety briefing prior to the installation and operation of the XCEM. This briefing will include a description of emergency operating procedures (i.e., in case of fire, tornado, laboratory accident) and identification and location and operation of safety equipment (e.g. fire alarms, fire extinguishers, eye washes, exits. Test participants are required

R5-2014-0104710000365

to wear hearing protection. Steel-toed safety shoes and work gloves are recommended. Eye wear is not required.

10.0 REFERENCES

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EPA. (1991). U.S. EPA Method 301 Field Validation of Emission Concentrations from Stationary Sources. Federal Register Vol. 56, No. 114. June 13, 1991.

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R5-2014-0104710000365

Appendix B: Determination of XCEM Reported Concentrations 2001

XCEM Metal Concentration Determination

To measure metal concentrations in stack gas, the XCEM uses an Aalborg mass flow controller to obtain flow rates and a QuanX energy dispersive x-ray fluorescence (XRF) analyzer to determine mass concentrations. The QuanX reported mass concentrations are then divided by the total dry flow to obtain concentrations in micrograms per dry standard cubic meter . The entire process is automated by a custom WonderWare® software interface. The original concentrations reported during the 2001 test are shown in Table B1.

Test data were modified according to a final post-test calibration and evaluation of dryer capabilities resulting in an 8 percent increase in reported metal concentrations. All calibration adjustments were completed prior to receiving M29 results. The final reported concentrations with the 8 percent correction are shown in **XCEM Reported Concentrations** (page 15).

Global Corrections to Reported Concentrations

Flow Corrections

For the TEAD validation testing, the mass flow meter was cross-checked with a Sierra mass flow meter and was determined to be in good agreement. For this reason, no changes were made to flow measurements applied to reported concentrations.

Mass Corrections

Due to the rapid turn-around time required for this project (6 weeks between contract award date and delivery date), a final XRF calibration was not conducted until after the tests. The XCEM is calibrated with thin-film standards produced by the National Institute of Standards and Testing (NIST) and Micro-

R5-2014-0104710000365

Matter Inc. (Deer Harbor, WA). These standards, which are 47-mm in diameter, are larger than the x-ray beam intensity area. In contrast, the exposed spot on the XCEM filter is about 7 mm in diameter and is smaller than the x-ray beam intensity area. A global conversion factor is required to convert intensities from thin film to spot size. During the final calibration it was determined that a global increase of 4.4 percent was required to better account for the thin-film to spot conversion factor.

Dryer Inefficiency Corrections

The XCEM uses a gas dryer built by Universal Analyzer of Reno, NV. The dryer cools gas to a predefined temperature, which condenses the water in the gas stream. Water is then removed from the dryer using a pneumatic pump. Following the test, it was determined that manufacturer specifications were not properly defined for the partial vacuum in the XCEM. CES conducted extensive testing on the gas dryer (Table B2) and determined that, under a partial vacuum, the XCEM had 3.5 percent water content. For this reason, the XCEM concentrations were increased uniformly by 3.5 percent.

R5-2014-0104710000365

Table B1. Original XCEM reported concentrations (µg/dscm) uncorrected for calibration and dryer changes.

Date	Start	Stop	XC No.	RM No.	XC Time (min)	As	Ba	Cd	Cr	Hg	Ni	Pb	Sb	Zn
5/14/01	10:45	11:05	650	Run 1	19:48.0	74.2	153	25.7	2.8	55	318	1,020	314	275
5/14/01	11:05	11:26	651	Run 1	21:12.0	78.6	158	24.0	2.3	101	403	1,043	345	293
5/14/01	11:26	11:48	652	Run 1	21:32.0	76.8	178	24.5	1.7	145	432	1,064	334	296
5/14/01	11:48	12:09	653	Run 1	21:42.0	78.8	153	20.2	2.0	192	415	1,107	327	292
5/14/01	12:10	12:31	654	Run 1	21:41.0	89.1	174	26.1	2.4	224	435	1,221	349	317
5/14/01	12:31	12:53	655	Run 1	21:51.0	99.9	202	29.5	2.0	238	477	1,487	369	344
5/14/01	12:53	13:15	656	Run 1	22:07.0	57.4	187	25.2	2.2	262	428	656	358	322
Average					**21:24.7**	**79.2**	**172**	**25.0**	**2.2**	**174**	**416**	**1,086**	**342**	**306**
SD						**13.1**	**18**	**2.8**	**0.4**	**76**	**49**	**249**	**19**	**23**
RSD						**17**	**11**	**11**	**16**	**44**	**12**	**23**	**5**	**8**
5/14/01	13:58	14:23	659	Run 2	25:09.0	177.3	213	24.8	2.2	172	347	3,168	333	277
5/14/01	14:23	14:46	660	Run 2	22:56.0	165.0	207	27.3	1.9	217	395	3,007	351	320
5/14/01	14:46	15:09	661	Run 2	22:56.0	162.3	230	24.1	1.1	226	395	2,793	368	325
5/14/01	15:09	15:32	662	Run 2	22:54.0	155.7	231	20.7	1.9	204	375	2,484	342	307
5/14/01	15:32	15:55	663	Run 2	22:36.0	146.1	180	27.0	1.1	221	384	2,173	351	321
5/14/01	15:55	16:17	664	Run 2	22:34.0	25.5	159	25.1	2.4	238	363	168	322	295
Average					**23:10.8**	**138.6**	**203**	**24.8**	**1.8**	**213**	**377**	**2,299**	**345**	**307**
SD						**56.4**	**29**	**2.4**	**0.5**	**23**	**19**	**1,104**	**16**	**19**
RSD						**41**	**14**	**10**	**30**	**11**	**5**	**48**	**5**	**6**
5/14/01	17:00	17:23	667	Run 3	22:45.0	20.0	117	23.5	3.1	240	366	110	309	297
5/14/01	17:23	17:44	668	Run 3	21:00.0	16.6	130	19.7	2.0	244	359	84	310	295
5/14/01	17:44	18:05	669	Run 3	20:52.0	15.0	146	25.0	2.4	246	386	55	329	315
5/14/01	18:05	18:26	670	Run 3	20:58.0	14.9	162	26.8	2.6	248	379	51	336	314
5/14/01	18:26	18:47	671	Run 3	20:53.0	16.2	155	19.8	2.3	236	383	56	326	308
5/14/01	18:47	19:07	672	Run 3	20:54.0	13.6	136	22.2	2.2	230	383	60	333	321
Average					**21:13.7**	**16.0**	**141**	**22.8**	**2.4**	**241**	**376**	**69**	**324**	**308**
SD						**2.2**	**17**	**2.8**	**0.4**	**7**	**11**	**23**	**12**	**11**
RSD						**14**	**12**	**12**	**16**	**3**	**3**	**33**	**4**	**3**
5/15/01	8:59	9:18	684	Run 4	19:43.0	15.6	134	19.9	4.1	31	273	63	251	218
5/15/01	9:18	9:39	685	Run 4	20:34.0	17.3	161	26.4	5.8	50	371	64	308	295
5/15/01	9:39	10:00	686	Run 4	20:55.0	17.7	124	30.7	5.0	64	400	61	335	323
5/15/01	10:00	10:21	687	Run 4	21:00.0	18.2	142	28.3	4.9	74	400	60	343	322
5/15/01	10:21	10:42	688	Run 4	20:58.0	18.5	176	29.7	4.7	78	401	59	350	319
5/15/01	10:42	11:03	689	Run 4	20:57.0	16.8	134	24.7	4.8	79	387	51	334	314
5/15/01	11:03	11:24	690	Run 4	20:51.0	18.3	170	26.4	5.1	90	412	41	351	339
Average					**20:42.6**	**17.5**	**149**	**26.6**	**4.9**	**67**	**378**	**57**	**325**	**304**
SD						**1.0**	**20**	**3.6**	**0.5**	**20**	**48**	**8**	**36**	**40**
RSD						**6**	**14**	**14**	**10**	**30**	**13**	**14**	**11**	**13**
5/15/01	12:06	12:27	693	Run 5	20:55.0	19.1	164	29.0	5.1	86	408	46	354	328
5/15/01	12:27	12:48	694	Run 5	20:52.0	17.7	159	31.2	5.1	90	398	50	343	322
5/15/01	12:48	13:09	695	Run 5	20:51.0	17.4	141	31.8	5.6	94	386	48	335	314
5/15/01	13:09	13:30	696	Run 5	20:48.0	18.4	168	31.0	4.9	106	416	43	357	333
5/15/01	13:30	13:51	697	Run 5	20:57.0	15.4	171	33.2	5.3	113	416	42	364	338
5/15/01	13:51	14:12	698	Run 5	20:59.0	17.6	168	29.8	5.0	120	411	35	361	331
Average					**20:53.7**	**17.6**	**162**	**31.0**	**5.2**	**101**	**406**	**44**	**352**	**328**
SD						**1.2**	**11**	**1.5**	**0.3**	**13**	**12**	**5**	**11**	**8**
RSD						**7**	**7**	**5**	**5**	**13**	**3**	**12**	**3**	**3**
5/15/01	14:54	15:15	701	Run 6	20:57.0	18.4	153	29.1	5.0	127	422	36	363	348
5/15/01	15:15	15:36	702	Run 6	20:59.0	16.3	140	29.5	5.0	135	431	36	358	350
5/15/01	15:36	15:57	703	Run 6	20:58.0	13.9	155	29.1	5.0	132	410	45	358	335
5/15/01	15:57	16:18	704	Run 6	20:56.0	14.3	153	29.0	5.5	130	398	44	344	324
5/15/01	16:18	16:39	705	Run 6	20:54.0	14.8	173	31.6	4.9	155	395	34	352	326
5/15/01	16:39	17:00	706	Run 6	20:55.0	15.9	171	30.4	5.1	152	409	33	360	336
5/15/01	17:00	17:21	707	Run 6	20:58.0	15.0	152	34.0	5.7	154	428	42	359	342
Average					**20:56.7**	**15.5**	**157**	**30.4**	**5.2**	**141**	**413**	**38**	**356**	**337**
SD						**1.5**	**12**	**1.9**	**0.3**	**13**	**14**	**5**	**6**	**10**
RSD						**10**	**7**	**6**	**6**	**9**	**3**	**13**	**2**	**3**

R5-2014-0104710000365

Table B1 (Cont'd). Original XCEM reported concentrations (μg/dscm) uncorrected for calibration and dryer changes.

5/15/01	18:03	18:24	710	Run 7	20:55.0	17.9	169	33.0	5.4	143	442	42	367	357
5/15/01	18:24	18:45	711	Run 7	20:58.0	19.3	154	31.9	5.9	124	443	41	374	366
5/15/01	18:45	19:06	712	Run 7	20:58.0	17.5	177	26.7	5.6	111	455	42	349	349
5/15/01	19:06	19:27	713	Run 7	20:59.0	16.9	155	28.6	5.2	112	425	37	347	332
5/15/01	19:27	19:48	714	Run 7	20:50.0	16.6	162	28.4	5.3	122	388	31	340	312
5/15/01	19:48	20:09	715	Run 7	20:41.0	15.5	148	30.8	5.1	127	404	28	351	325
Average					**20:53.5**	**17.3**	**161**	**29.9**	**5.4**	**123**	**426**	**37**	**355**	**340**
SD						**1.3**	**11**	**2.4**	**0.3**	**12**	**26**	**6**	**13**	**21**
RSD						**7**	**7**	**8**	**6**	**10**	**6**	**16**	**4**	**6**
5/16/01	8:58	9:18	725	Run 8	20:24.0	30.7	103	30.1	4.8	15	178	268	130	124
5/16/01	9:18	9:39	726	Run 8	20:33.0	30.8	128	29.5	5.5	19	204	224	124	139
5/16/01	9:39	10:00	727	Run 8	20:33.0	26.8	134	29.9	5.0	20	205	214	116	140
5/16/01	10:00	10:20	728	Run 8	20:33.0	26.6	145	27.2	4.9	26	183	184	126	137
5/16/01	10:20	10:41	729	Run 8	20:26.0	21.7	163	33.6	4.7	31	189	187	125	130
5/16/01	10:41	11:01	730	Run 8	20:24.0	28.6	141	30.2	5.3	33	200	209	124	139
5/16/01	11:01	11:22	731	Run 8	20:30.0	26.5	150	30.0	5.3	40	209	199	130	139
Average					**20:29.0**	**27.4**	**138**	**30.1**	**5.1**	**26**	**195**	**212**	**125**	**135**
SD						**3.1**	**19**	**1.9**	**0.3**	**9**	**12**	**29**	**5**	**6**
RSD						**11**	**14**	**6**	**6**	**34**	**6**	**14**	**4**	**4**
5/16/01	11:42	12:03	733	Run 9	20:28.0	29.0	169	30.6	4.1	45	195	176	126	136
5/16/01	12:03	12:23	734	Run 9	20:26.0	22.2	157	30.3	5.2	46	186	158	129	131
5/16/01	12:23	12:44	735	Run 9	20:21.0	25.5	142	28.5	4.9	45	189	150	132	136
5/16/01	12:44	13:04	736	Run 9	20:18.0	24.9	191	32.8	6.0	52	206	177	143	141
5/16/01	13:04	13:25	737	Run 9	20:24.0	23.2	132	28.8	4.8	50	199	140	134	134
5/16/01	13:25	13:45	738	Run 9	20:19.0	24.8	127	26.6	4.8	54	185	141	134	133
5/16/01	13:45	14:05	739	Run 9	20:23.0	22.5	139	27.0	4.8	56	211	144	137	132
Average					**20:22.7**	**24.6**	**151**	**29.2**	**5.0**	**50**	**196**	**155**	**133**	**135**
SD						**2.3**	**23**	**2.2**	**0.5**	**4**	**10**	**16**	**6**	**3**
RSD						**9**	**15**	**7**	**11**	**9**	**5**	**10**	**4**	**2**
5/16/01	14:46	15:07	742	Run 10	20:24.0	25.0	144	32.1	5.5	85	194	135	137	135
5/16/01	15:07	15:27	743	Run 10	20:21.0	33.7	174	34.2	5.0	83	200	242	142	139
5/16/01	15:27	15:48	744	Run 10	20:23.0	21.4	130	30.0	5.0	76	178	106	124	123
5/16/01	15:48	16:08	745	Run 10	20:16.0	22.5	178	29.2	5.0	84	193	124	135	138
5/16/01	16:08	16:28	746	Run 10	20:21.0	21.6	149	33.5	5.1	88	192	100	151	135
5/16/01	16:29	16:49	747	Run 10	20:20.0	21.6	154	28.6	5.2	88	188	88	130	127
5/16/01	16:49	17:09	748	Run 10	20:20.0	17.3	129	27.7	5.0	101	173	102	141	127
Average					**20:20.7**	**23.3**	**151**	**30.8**	**5.1**	**86**	**188**	**128**	**137**	**132**
SD						**5.1**	**19**	**2.5**	**0.2**	**8**	**10**	**53**	**9**	**6**
RSD						**22**	**13**	**8**	**4**	**9**	**5**	**41**	**6**	**5**

R5-2014-0104710000365

Table B1 (Cont'd). Original XCEM reported concentrations (μg/dscm) uncorrected for calibration and dryer changes.

5/16/01	17:32	17:52	750	Run 11	20:21.0	19.9	165	28.9	5.5	94	195	100	139	132
5/16/01	17:52	18:12	751	Run 11	20:18.0	19.7	136	28.0	4.8	89	193	94	136	130
5/16/01	18:12	18:33	752	Run 11	20:20.0	19.5	157	27.2	4.9	88	189	96	130	135
5/16/01	18:33	18:53	753	Run 11	20:18.0	19.7	165	27.9	5.0	88	178	84	136	128
5/16/01	18:53	19:13	754	Run 11	20:12.0	20.4	141	24.4	5.3	89	177	82	136	131
5/16/01	19:13	19:34	755	Run 11	20:12.0	20.3	155	30.3	5.1	86	186	82	132	135
5/16/01	19:34	19:54	756	Run 11	20:17.0	18.7	141	30.7	4.2	78	196	89	136	135
Average					**20:16.9**	**19.7**	**151**	**28.2**	**5.0**	**87**	**188**	**90**	**135**	**132**
SD						**0.6**	**12**	**2.1**	**0.4**	**5**	**8**	**7**	**3**	**3**
RSD						**3**	**8**	**8**	**8**	**6**	**4**	**8**	**2**	**2**
5/17/01	11:12	11:32	770	Run 12	20:01.0	25.0	161	24.6	3.8	22	208	157	127	123
5/17/01	11:32	11:52	771	Run 12	20:08.0	27.4	181	21.5	3.9	33	221	215	147	135
5/17/01	11:52	12:12	772	Run 12	20:14.0	32.6	161	28.2	4.0	51	206	253	153	146
5/17/01	12:12	12:32	773	Run 12	20:16.0	25.6	210	22.6	3.7	68	205	189	146	149
5/17/01	12:32	12:53	774	Run 12	20:12.0	25.1	141	29.3	4.4	73	190	149	146	140
5/17/01	12:53	13:13	775	Run 12	20:12.0	18.2	164	25.9	4.1	77	189	127	144	133
5/17/01	13:13	13:33	776	Run 12	20:07.0	20.0	138	26.1	3.8	80	177	129	144	140
Average					**20:10.0**	**24.9**	**165**	**25.4**	**4.0**	**58**	**199**	**174**	**144**	**138**
SD						**4.7**	**24**	**2.8**	**0.2**	**23**	**15**	**47**	**8**	**9**
RSD						**19**	**15**	**11**	**6**	**40**	**7**	**27**	**6**	**6**
5/17/01	14:14	14:34	779	Run 13	20:15.0	23.6	150	33.3	4.7	74	186	110	158	136
5/17/01	14:34	14:54	780	Run 13	20:10.0	24.5	194	31.3	4.9	74	197	113	157	135
5/17/01	14:54	15:14	781	Run 13	20:09.0	21.9	147	33.4	5.6	76	217	109	155	138
5/17/01	15:14	15:34	782	Run 13	20:10.0	24.3	129	31.3	5.4	77	197	103	157	138
5/17/01	15:35	15:55	783	Run 13	20:12.0	26.2	182	37.6	5.4	77	160	119	157	109
5/17/01	15:55	16:15	784	Run 13	20:02.0	23.8	153	36.2	5.6	69	157	112	154	76
5/17/01	16:15	16:35	785	Run 13	19:57.0	12.0	87	17.3	3.7	42	65	79	71	20
Average					**20:07.9**	**22.3**	**149**	**31.5**	**5.0**	**70**	**168**	**107**	**144**	**107**
SD						**4.7**	**35**	**6.7**	**0.7**	**12**	**50**	**13**	**32**	**45**
RSD						**21**	**24**	**21**	**14**	**18**	**30**	**12**	**22**	**42**

Table B2. Results of dryer tests.

Day	Time (min)	Flow actual (sLpm)	Pressure in line (psia)	Web Bulb Temp (°F)	Vol of air/water (L)	Mass of Water Collected (g)	Vol of Water (L)	Impinger % water by vol
1	270	0.82	7.3	150	220.4	7.9	9.8	4.5
2	200	0.82	7.3	150	163.3	4.7	5.8	3.6
3	78	0.84	7.3	120	65.5	1.8	2.2	3.4
4	126	0.83	7.3	168	104.6	2.8	3.5	3.3

R5-2014-0104710000365

Appendix C: Transport and Calibration Evaluations

Quantitative Spike Injection by CES

CES Spiking Test Design

Following calibration, a series of 11 tests were conducted at TEAD to certify the calibration and check the ability of the XCEM to transport particulates from the top of the shed to the filter tape. The tests included quantitative spiking of various aerosolized metals into the XCEM transport line immediately prior to entering the shed. The metals were then sampled by the XCEM. The rest of the spiked aerosol, about 99 percent of the volume, was sampled by two filters downstream of the stilling chamber as illustrated in Figure C1.

CES used a Quantitative Spike Injection System (QSIS) to conduct the tests. The QSIS includes an atomizer and a drying chamber that generate a simulated stack gas containing the metals of interest in ~100 ppm of nitric acid. Two pumps pulled 80-100 sLpm of the simulated stack gas through the atomization system and XCEM stilling chamber. Approximately 1 percent of the simulated stack gas was sampled and analyzed by the XCEM. The remaining gas was transported out of the XCEM stilling chamber into a manifold containing two filter holders. The upstream filter holder contained a 47-mm-diameter membrane filter (MF) while the downstream holder held a 47-mm-diameter quartz fiber filter (QFF). After each test, the metal concentrations on the two filters were determined using a QuanX XRF, and their total mass, identified as the "Total Capture" concentration, was compared to the theoretical atomization concentration and reported XCEM concentrations.

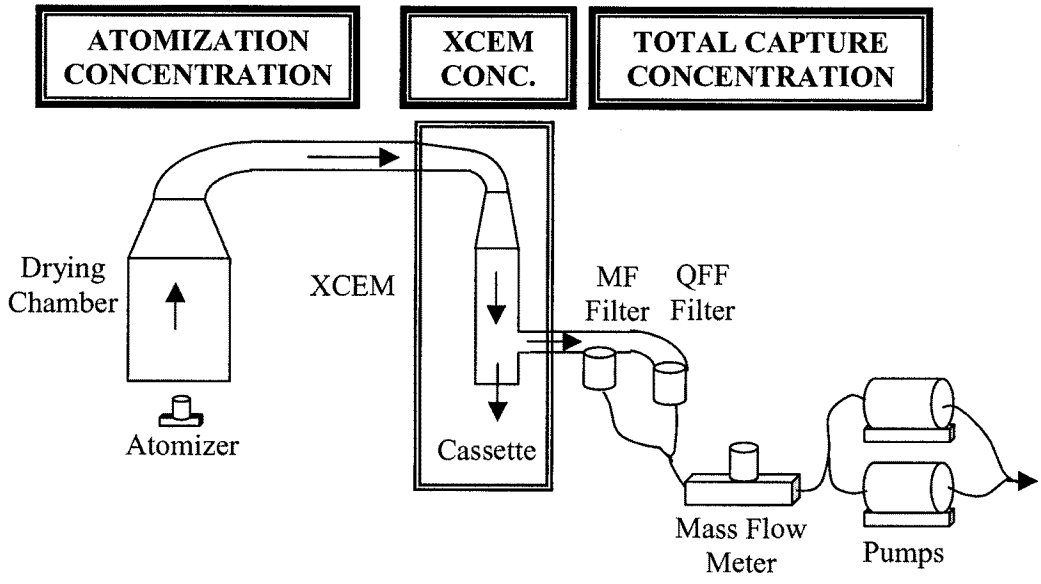

Figure C1. Experimental design for atomization tests.

Test design for atomization of Pb and Cr (Tests 1–3)

Three tests were conducted using a solution of Pb and Cr nitrates in 5 percent nitric acid. The injected solution had a concentration of 25.4 µg/mL of Pb and 25.1 µg/mL of Cr. Atomizer concentrations were determined by weighing the solution before and after testing and multiplying the net atomized mass by the concentration to determine total micrograms of metal emitted during the test. This mass was compared to the total mass on the resin-impregnated and quartz fiber filters (RIF and QFF) located downstream of the XCEM.

During these tests, the XCEM reported values every 20 minutes and completed 30 runs. Atomization chamber and total capture filter temperatures were maintained at about 140 °F while the stilling chamber and cassette were maintained at about 225 °F. The mainline flow varied between 88-97 sLpm and the XCEM sampled 0.8 sLpm.

Following the first test, a leak was discovered in the system, so the first test was disregarded and a third test was conducted. Data from the first test are included in Appendix C, but were not used to evaluate the calibration.

Test design for atomization of As, Cd, Cr, Ba, Hg, Pb, Se, and Ag (Tests 4–7)

A second series of four tests was conducted using a NIST traceable stock solution of As, Cd, Cr, Ba, Hg, Pb, Se, and Ag (VHG Labs, Inc., Manchester, NH). All eight elements were at the same concentration in the stock solution. Two sets of

duplicate runs were conducted with nominal concentrations at about 250 µg/m³ for tests 4 and 5 and 125 µg/m³ for tests 6 and 7. Atomization and XCEM temperature and flow conditions were the same as for the Pb and Cr tests. The XCEM reported values every 20 minutes and completed an additional 30 runs.

Test design for atomization of Cd, Ba, Hg, Ni, Pb, and Zn (Tests 8-11)

The third series of tests used a NIST traceable VHG stock solution of Cd, Ba, Hg, Ni, Pb, and Zn. Two sets of duplicate runs were conducted with concentrations from runs 8 and 9 cut in half for runs 10 and 11. Atomization and XCEM temperature and flow conditions were the same as for the Pb and Cr test. The XCEM reported values every 20 minutes and completed an additional 35 runs during these tests.

CES Spiking Test Results

Atomization vs. XCEM

Before and after atomization, the spike injection solution was weighed to determine net change in mass. This mass was divided by the time and flow to determine atomization rate in micrograms per dry standard cubic meter as shown in equation 6:

$$C_k = \frac{(m_i - m_f) \cdot a_k}{d \cdot f \cdot t} \cdot 10^6 \qquad \textbf{[Eq 6]}$$

where:

C_k = Gas concentration for element "k" during a test
m_i = Initial mass of atomized solution (g)
m_f = Final mass of atomized solution (g)
d = Density of solution (g/mL)
a_k = Concentration of element "k" in solution (g of element k/mL of solution)
t = Time (min)
f = Gas flow rate (dscm/min)

Data used to calculate predicted metals concentrations based on atomization rates are shown in Table C1. Atomization rate predictions vs. XCEM measured concentrations are shown in Table C2.

R5-2014-0104710000365

Table C1. Flow rates and concentrations used to calculate atomization concentrations.

Test	Atom. vol (ml)	As	Cd	Fe	Cr	Ba	Hg	Ni	Pb	Sb	Se	Ag	Zn	Ti
	ml	µg/ml	µg/ml	µg/ml	µg/ml	µg/ml	µg/ml	µg/ml	µg/ml	µg/ml	µg/ml	µg/ml	µg/ml	µg/ml
1	56.1				25.1				25.4					
2	31.9				25.1				25.4					
3	41.8				25.1				25.4					
4	30.3	50.6	50.6		50.6	50.6	50.6		50.6		50.6	50.6		
5	37.8	50.6	50.6		50.6	50.6	50.6		50.6		50.6	50.6		
6	35.5	25.1	25.1		25.1	25.1	25.1		25.1		25.1	25.1		
7	32.9	25.1	25.1		25.1	25.1	25.1		25.1		25.1	25.1		
8	32.1		17.4			497.7		99.6	29.9				99.6	
9	31.3		17.4			497.7		99.6	29.9				99.6	
10	36.2		8.6			246.9		49.4	14.8				49.4	
11	33.2		8.6			246.9		49.4	14.8				49.4	

Table C2. Atomization vs. XCEM concentrations.

TEST	AS			CD			CR			BA			HG		
	XC	AT	XC/AT	XC	AT	XC/AT	XC	AT	XC/AT	XC	AT	XC/AT	XC	AT	XC/AT
	µg/DSCM			µg/DSCM			µg/DSCM			µg/DSCM			µg/DSCM		
2							122	106	1.15						
3							126	112	1.12						
4	245	230	1.07	201	230	0.87	260	230	1.13	247	230	1.07	226	230	0.98
5	230	234	0.98	192	234	0.82	243	234	1.04	247	234	1.06	218	234	0.93
6	126	126	1.00	105	126	0.83	137	126	1.09	158	126	1.26	120	126	0.95
7	123	122	1.00	97	122	0.79	126	122	1.03	153	122	1.25	112	122	0.92
8				63	76	0.82				2384	2183	1.09	50	87	0.57
9				54	66	0.81				2022	1901	1.06	41	76	0.54
10				32	38	0.84				1265	1101	1.15	20	44	0.45
11				33	40	0.82				1214	1152	1.05	28	46	0.61
AVG.	**181**	**178**	**1.01**	**97**	**117**	**0.83**	**169**	**155**	**1.09**	**961**	**881**	**1.12**	**102**	**121**	**0.75**

TEST	NI			PB			SE			AG			ZN		
	XC	AT	XC/AT	XC	AT	XC/AT	XC	AT	XC/AT	XC	AT	XC/AT	XC	AT	XC/AT
	µg/DSCM			µg/DSCM			µg/DSCM			µg/DSCM			µg/DSCM		
2				111	107	1.04									
3				117	113	1.03									
4				266	230	1.16	236	230	1.03	217	230	0.94			
5				247	234	1.06	221	234	0.94	204	234	0.87			
6				137	126	1.09	122	126	0.97	113	126	0.90			
7				121	122	0.99	117	122	0.96	102	122	0.84			
8	450	437	1.03	133	131	1.01							463	437	1.06
9	383	380	1.01	114	114	1.00							394	380	1.04
10	243	220	1.10	73	66	1.10							249	220	1.13
11	226	230	0.98	67	69	0.96							233	230	1.01
AVG.	**326**	**317**	**1.03**	**138**	**131**	**1.04**	**174**	**178**	**0.97**	**159**	**178**	**0.89**	**335**	**317**	**1.06**

Reported XCEM concentrations matched expected atomization values for As (101 percent), Cr (109 percent), Ni (103 percent), Pb (104 percent), Ba (112 percent), Se (97 percent), and Zn (106 percent). Mercury XCEM concentrations matched atomization rates for runs 4–7 (95 percent), but were low for runs 8–11 (54 percent). During runs 8–11, the outside air temperature dropped dramatically and

R5-2014-0104710000365

snow was on the transport line. For this reason, the Hg numbers for runs 8–11 were considered less reliable.

Both Cd and Ag were low by 10–15 percent relative to the expected concentrations. This difference was either caused by transport inefficiency or calibration error. To determine which source created the discrepancy, a comparison was made of the Cd/Ag concentrations relative to other elements captured downstream of the XCEM. The results of these comparisons are discussed in the next section.

Total capture vs. XCEM

The total flow used for atomization was captured downstream of the XCEM on an MF and QFF. These filters were then analyzed at CES and compared to the atomized concentrations. The total capture system is downstream of a 90° elbow and is not expected to be quantitative; however, the relative concentrations of the elements should stay constant. Table B3 shows the total micrograms atomized vs. the total captured downstream of the XCEM. Reported Cr concentrations have not been corrected for filter absorption, which can be significant on a QFF. In this table, it can be seen that the transport efficiency to the filters was dependent on the injection solution. For tests 2 and 3, the transport was about 90 percent for Pb. The second solution was used for tests 4 through 7, with a resulting transport efficiency of about 85 percent for As, Cd, Ni, Pb, and Se.

Except for Hg, which can form a vapor, the atomization process results in particles that contain metals in proportion to their concentration in the original solution. Because the elements associated with particles should be in proportion to the solution, the results in Table C3 were normalized to Pb to determine relative transport efficiencies. These results are shown in Table C4. Both Cd and Ag in Table C4 show good agreement with Pb, arsenic, and the other elements. Thus, it appears that Cd and Ag were transported with the other elements. From these data, it was concluded that the significant difference between Cd/Ag and the other elements in Table C2 was not due to transport inefficiency but rather the result of calibration error.

R5-2014-0104710000365

Table C3. Total capture mass (TC) vs. atomization mass (AT).

Test	As			Cd			Cr			Ba			Hg		
	TC	AT	FIL/TC	TC	AT	FIL/TC	TC	AT	FIL/TC	TC	AT	FIL/TC	TC	AT	FIL/TC
	µg			µg			µg			µg			µg		
2							700	821	0.85						
3							791	1077	0.73						
4	1192	1574	0.76	1192	1574	0.76	917	1574	0.58	1461	1574	0.93	1013	1574	0.64
5	1535	1963	0.78	1530	1963	0.78	1145	1963	0.58	1884	1963	0.96	1402	1963	0.71
6	807	914	0.88	781	914	0.85	662	914	0.72	948	914	1.04	689	914	0.75
7	702	848	0.83	682	848	0.80	571	848	0.67	832	848	0.98	642	848	0.76
8				454	572	0.79				14746	16374	0.90			
9				446	559	0.80				14631	15976	0.92			
10				286	320	0.89				9142	9158	1.00			
11				218	294	0.74				7263	8418	0.86			
AVG.	1059	1325	0.81	699	881	0.80	850	1235	0.71	6363	6903	0.95	937	1325	0.72

Test	Ni			Pb			Se			Ag			Zn		
	TC	AT	FIL/TC	TC	AT	FIL/TC	TC	AT	FIL/TC	TC	AT	FIL/TC	TC	AT	FIL/TC
	µg			µg			µg			µg			µg		
2				760	831	0.91									
3				970	1090	0.89									
4				1258	1574	0.80	1196	1574	0.76	1295	1574	0.82			
5				1622	1963	0.83	1550	1963	0.79	1667	1963	0.85			
6				837	914	0.92	806	914	0.88	847	914	0.93			
7				728	848	0.86	702	848	0.83	741	848	0.87			
8	1952	3277	0.60	724	984	0.74							1979	3277	0.60
9	1906	3197	0.60	713	960	0.74							1933	3197	0.60
10	1421	1833	0.78	463	550	0.84							1394	1833	0.76
11	1139	1685	0.68	369	506	0.73							1140	1685	0.68
AVG.	1604	2498	0.66	887	1062	0.83	1064	1325	0.81	1138	1325	0.87	1611	2498	0.66

Table C4. Lead normalized atomization mass (AT) vs. total capture (TC).

Test	As			Cd			Cr			Ba			Hg		
	TC	AT	TC/AT	TC	AT	TC/AT	TC	AT	TC/AT	TC	AT	TC/AT	TC	AT	TC/AT
2							0.92	0.99	0.93						
3							0.82	0.99	0.83						
4	0.95	1.00	0.95	0.95	1.00	0.95	0.73	1.00	0.73	1.16	1.00	1.16	0.80	1.00	0.80
5	0.95	1.00	0.95	0.94	1.00	0.94	0.71	1.00	0.71	1.16	1.00	1.16	0.86	1.00	0.86
6	0.96	1.00	0.96	0.93	1.00	0.93	0.79	1.00	0.79	1.13	1.00	1.13	0.82	1.00	0.82
7	0.96	1.00	0.96	0.94	1.00	0.94	0.78	1.00	0.78	1.14	1.00	1.14	0.88	1.00	0.88
8				0.63	0.58	1.08				20.4	16.6	1.22			
9				0.63	0.58	1.08				20.5	16.6	1.23			
10				0.62	0.58	1.06				19.7	16.6	1.19			
11				0.59	0.58	1.02				19.7	16.6	1.18			
AVG.	**0.96**	**1.00**	**0.96**	**0.78**	**0.79**	**1.00**	**0.79**	**1.00**	**0.79**	**10.6**	**8.8**	**1.18**	**0.84**	**1.00**	**0.84**

Test	Ni			Pb			Se			Ag			Zn		
	TC	AT	TC/AT	TC	AT	TC/AT	TC	AT	TC/AT	TC	AT	TC/AT	TC	AT	TC/AT
2				1.00	1.00	1.00									
3				1.00	1.00	1.00									
4				1.00	1.00	1.00	0.95	1.00	0.95	1.03	1.00	1.03			
5				1.00	1.00	1.00	0.96	1.00	0.96	1.03	1.00	1.03			
6				1.00	1.00	1.00	0.96	1.00	0.96	1.01	1.00	1.01			
7				1.00	1.00	1.00	0.96	1.00	0.96	1.02	1.00	1.02			
8	2.70	3.33	0.81	1.00	1.00	1.00							2.73	3.33	0.82
9	2.67	3.33	0.80	1.00	1.00	1.00							2.71	3.33	0.81
10	3.07	3.33	0.92	1.00	1.00	1.00							3.01	3.33	0.90
11	3.09	3.33	0.93	1.00	1.00	1.00							3.09	3.33	0.93
AVG.	**2.88**	**3.33**	**0.87**	**1.00**	**1.00**	**1.00**	**0.96**	**1.00**	**0.96**	**1.02**	**1.00**	**1.02**	**2.89**	**3.33**	**0.87**

Evaluation of Stack Transport

Test Design

The QSIS tests just discussed in the previous section were able to effectively evaluate the XCEM calibration. Since the QSIS was injected at the top of the shed, however, more data were needed to determine the transport efficiency of the sample line from the stack to the shed. To evaluate the entire transport system and the responsiveness of the XCEM to munitions burning, a second series of tests were conducted from 30 April to 2 May in which the TEAD stack was spiked by MSE-TA for metals of interest while munitions were incinerated. An EPA Reference Method 17 (M17) type train was used to capture a representative stack sample of PM near the inlet of the XCEM stack probe. Results of the M17 tests were then compared with the concurrent XCEM concentrations.

XCEM Responsiveness to Munitions Destruction

During the stack spiking, TEAD conducted normal burning operations in which they were destroying 20 mm bullets and tracers. The bullets were observed by the XCEM to have significant quantities of Pb, Cd, and tin (Sn), while only Sn was observed in significant quantities during tracer incineration. These elements were not spiked by MSE-TA. As shown in Figure 38, the XCEM displayed good responsiveness to various types of ammunitions burning and stack operation approaches.

Figure C2 shows the XCEM relationship between Sn and Cd when bullets were being destroyed. The high correlation ($r^2 = 0.94$) indicates that the two elements were from the same source. A 75 to 90 percent decrease is seen in Cd and Pb when tracers are being burned while Sn remains unchanged. Follow up conversations with TEAD personnel indicated that the tracers did not contain Cd and Pb, but did contain Sn. Figure C2 also shows the impact of opening and closing the bypass valve each day, with concentrations exhibiting spikes during the short period that the bypass valve was open.

One of the intended uses of the XCEM is as a monitor to better understand control efficiencies. The data in Figure 38 were used to help TEAD personnel identify the sources of metals in the stack gas and better control the emissions. Following M29 testing, TEAD stack operators conducted tests in which they used the XCEM to determine that the metals emissions could be significantly reduced by completely cutting off the bypass system during operation.

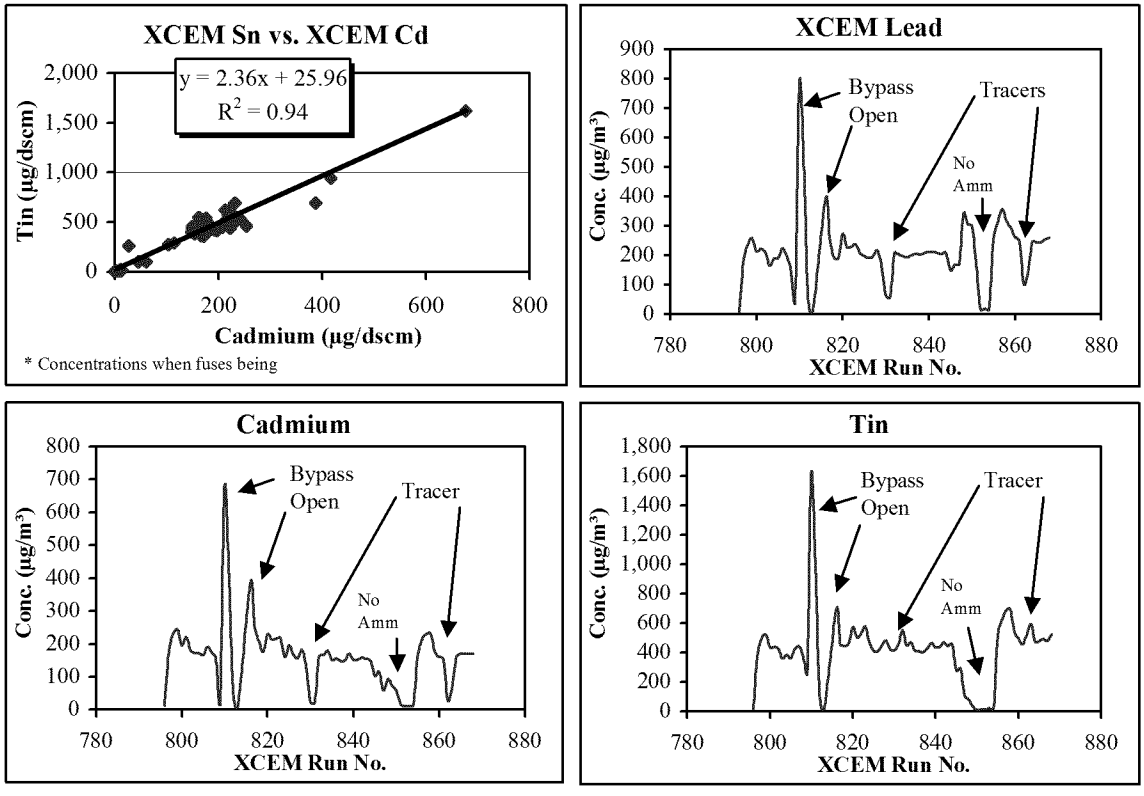

Figure C2. XCEM reported concentrations for nonspiked elements.

XCEM Response vs. MSE-TA Spiking

From 30 April to 2 May, MSE-TA spiked known concentrations of Ba, Hg, Ni, Sb, and Zn. The XCEM relative response to these concentrations is shown in Figure B3.

Other than Zn, which is associated with the incineration feed, the XCEM reported concentrations were slightly less than the MSE-TA predicted concentrations on 30 April and the morning of 1 May (runs 795–837). Following these runs, however, the transport line heat tracing was completed and the XCEM concentrations were within 5 to 15 percent of MSE-TA estimated concentrations.

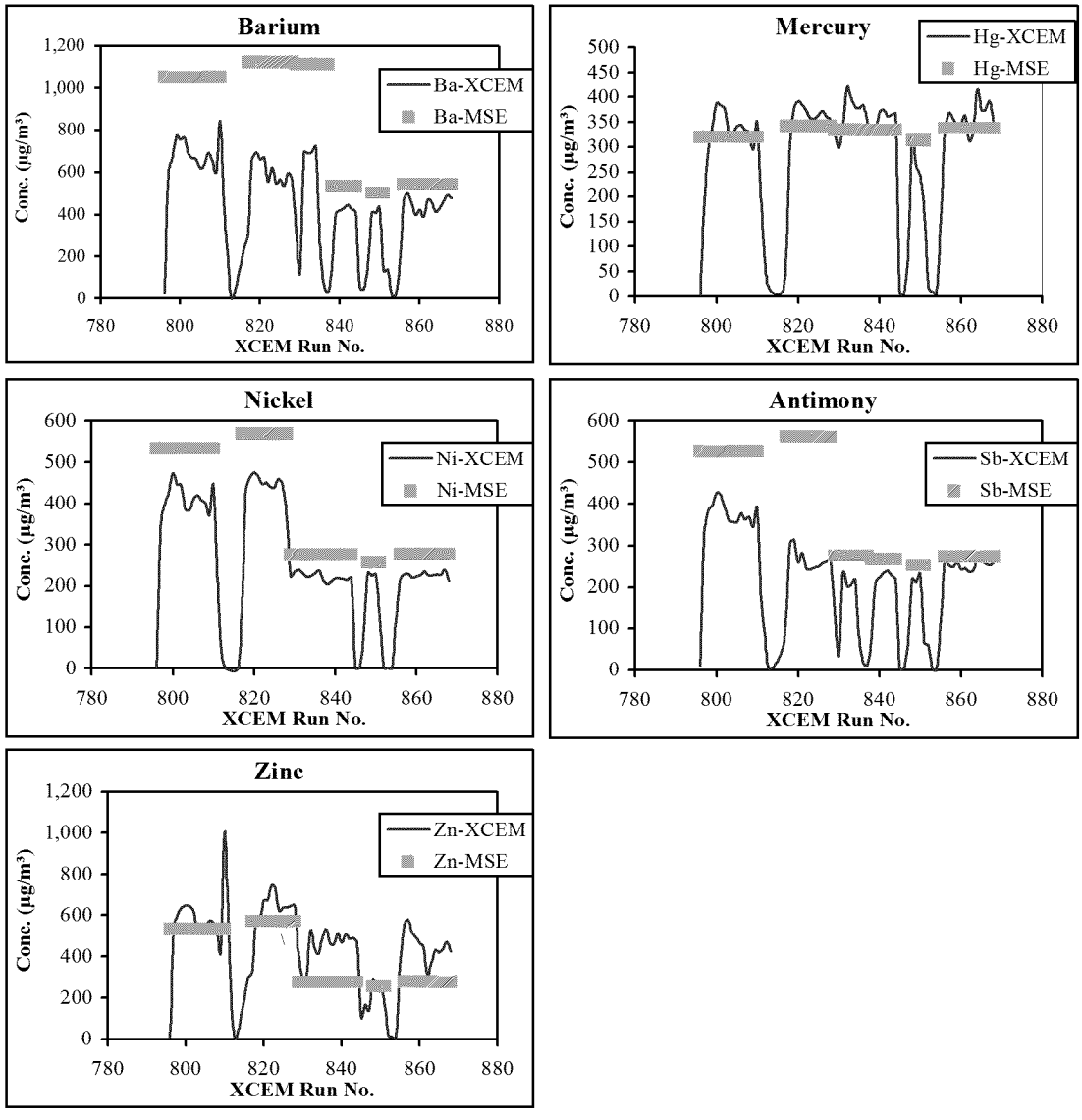

Figure C3. XCEM reported concentrations and MSE-projected concentrations for spiked elements.

XCEM Comparisons to Method 17 Results

To obtain adequate flows and meet stack temperature requirements, quartz fiber filters (QFF) were used for the in-stack filter holder for M17 testing. The QFFs cannot adequately trap Hg, but were analyzed for the spiked elements Ba, Ni, Zn, and Sb as well as the elements Cd and Pb, which were both found in the munitions. A total of 15 valid runs were conducted. Table C5 shows the results.

Both Ni and Zn were spiked together by MSE-TA. For these two metals, the XCEM to M17 ratios were 1.18 and 1.09, respectively. Since the XCEM was higher than M17, no indication of loss in the transport line was believed to have occurred. The uncertainty of the ratios was about 20–25 percent, which was

R5-2014-0104710000365

primarily the result of variability in the M17 flow measurement and uncertainties in M17 absorption corrections.

A second solution spiked by MSE-TA contained Ba and Sb. The two elements had respective XCEM to M17 ratios of 0.99 and 1.03, which indicated good transport efficiencies for elements in this spiked solution.

Although neither Pb nor Cd was spiked by MSE-TA, significant concentrations of both were found in the stack when bullets were being burned. The concentrations changed dramatically when tracers were burned instead of bullets for part of run 4. The XCEM and M17 were in good agreement for Pb, but the XCEM was significantly higher than M17 for Cd. The Cd results indicated a potential XCEM calibration error for Cd.

During the 3 days of testing, the Pd concentration, which is measured with every sample by the XCEM and indicates stability, varied from 90 to 105 percent. The higher than normal variability was determined to be associated with high ambient temperatures in the sample shed due to a faulty air conditioner. Installation of an improved temperature control system would help remedy this problem in the future.

Table C5. Method 17 vs. XCEM at TEAD.*

Run	Date	Start	Stop	Ba			Ni			Zn			Pb			Cd			Sb		
				XC	M17	X/M	XC	M17	X/M	XC	M17	X/M	XC	M17	X/M	XC	M17	X/M	XC	M17	X/M
1	4/30/02	3:11 PM	4:11 PM	650	716	0.91	401	301	1.33	552	466	1.18	192	208	0.92	176	134	1.31	363	348	1.04
2	5/1/02	8:36 AM	9:42 AM	567	677	0.84	448	363	1.23	674	595	1.13	213	239	0.89	192	158	1.21	248	258	0.96
3	5/1/02	10:02 AM	10:47 AM	471	605	0.78	313	284	1.10	539	548	0.98	194	222	0.87	159	134	1.19	214	238	0.90
4	5/1/02	11:00 AM	11:45 AM	544	533	1.02	236	177	1.33	353	302	1.17	99	99	0.99	58	43	1.36	173	138	1.25
5	5/1/02	12:01 PM	12:26 PM	708	859	0.82	222	230	0.97	430	459	0.94	200	257	0.78	171	161	1.06	210	207	1.02
6	5/1/02	12:43 PM	1:28 PM	131	104	1.25	231	186	1.24	506	450	1.12	198	202	0.98	153	122	1.25	38	35	1.08
7	5/1/02	1:46 PM	2:26 PM	281	348	0.81	208	196	1.06	487	504	0.97	205	236	0.87	161	141	1.14	144	158	0.91
8	5/1/02	2:40 PM	3:20 PM	432	642	0.67	218	246	0.88	495	591	0.84	210	248	0.85	154	151	1.02	232	293	0.79
9	5/1/02	3:35 PM	4:15 PM	416	515	0.81	217	217	1.00	477	528	0.90	207	238	0.87	152	142	1.07	221	257	0.86
10	5/2/02	8:41 AM	9:21 AM	419	362	1.16	226	160	1.42	269	199	1.35	307	220	1.40	70	48	1.45	220	168	1.31
11	5/2/02	11:05 AM	11:45 AM	476	333	1.43	219	149	1.47	555	446	1.24	331	273	1.21	220	151	1.45	254	167	1.52
12	5/2/02	12:12 PM	12:52 PM	410	518	0.79	221	231	0.96	485	510	0.95	279	275	1.02	169	150	1.13	251	238	1.06
13	5/2/02	1:07 PM	1:47 PM	446	346	1.29	230	168	1.37	359	268	1.34	150	108	1.38	70	50	1.42	239	151	1.59
14	5/2/02	2:33 PM	3:03 PM	451	541	0.83	227	237	0.96	432	487	0.89	244	258	0.95	171	145	1.17	259	554	0.47
15	5/2/02	3:10 PM	3:40 PM	487	331	1.47	229	165	1.39	453	325	1.40	256	174	1.47	170	107	1.58	254	383	0.66
Average				**459**	**495**	**0.99**	**256**	**221**	**1.18**	**471**	**445**	**1.09**	**219**	**217**	**1.03**	**150**	**122**	**1.25**	**221**	**239**	**1.03**
Standard Deviation						**0.26**			**0.20**			**0.18**			**0.22**			**0.17**			**0.30**

* XC and M17 concentrations in µg/dscm; XC = XCEM; X/M = XCEM/M17.

R5-2014-010471000365

R5-2014-0104710000365

Appendix D: Mercury Calibration and Loss Discussion 2002

Introduction

Mercury (Hg) represents a distinctly different hazardous element from the others included in these tests 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 Hg concentrations measured by the different methods compared in the 2002 test. This appendix discusses the details associated with both the adjustments that were made to the XCEM calibration factors and losses of Hg from particulate deposits after sample collection.

Calibration Adjustments

Two adjustments were made to the Hg results after the first M29 test run was started. The first adjustment was a 7 percent increase in the Hg sensitivity factor between M29 run 1 and run 2. The second was a 4 percent 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 Hg, which makes it difficult to make stable thin-film Hg standards. As such, thin film Hg 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 (XRF) sensitivity factors are a smoothly varying function of atomic number. This allows Hg sensitivity factors to be estimated by interpolation using well-defined sensitivity factors for elements with similar atomic number such as platinum, gold, thallium, lead (Pb), and bismuth. The following two adjustments were based on this interpolation process and a re-evaluation of the best-estimated calibration factor.

R5-2014-0104710000365

Adjustments During First Day of Testing

The XCEM underwent mercury calibration during preliminary spiking tests, prior to the M29 tests. During these spiking tests, the NIST thin-film standard for Pb was not available, and the Hg sensitivity was estimated based on a previous measurement of the Pb NIST standard. This fact was not realized until after the preliminary spiking testing started and a review of the preliminary Hg results indicated a potential bias relative to the NIST Pb results. As a result, the Hg calibration was adjusted by 7 percent at the earliest possible time, which was after M29 run 1 and before run 2.

Post-Test Adjustments

The second adjustment to the Hg results of 4 percent was applied when the calibration factors were reviewed following the M29 tests. A comparison with the ratio of Hg to Pb 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 percent correction was applied to the XCEM results prior to the submission of either the M29 or the XCEM results.

Losses From PM Fraction

The XCEM Hg results were, on average, 18 percent greater than the predicted concentration, 27 percent greater than the M29 results, 37 percent greater than the laboratory XRF measurements of the XCEM deposit spots, and 45 percent greater than cold vapor atomic absorption (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 Hg concentrations in the stack. It is hypothesized that the large differences between the XCEM Hg results and the results from the other methods is due to the loss of Hg from the filter deposits after the M29 and XCEM samples were collected and after the XCEM original measurements were made.

Model

A model has been developed to explain the apparent high XCEM Hg concentrations relative to M29. In this model, Hg 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 Hg was associated with the particulate fraction, and the Hg in this particulate was unstable. Since all of the other analytical methods relied on aged samples, the Hg concentration results were low due to

vaporization of particulate Hg prior to laboratory analysis. 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.

Experimental

The initial XCEM measurements were based on the analysis of filter deposits, which were a combination of both absorbed vapor phase Hg species and surface deposits of particulate Hg 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 were available for comparison with subsequently developed spectra.

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

- All of the XCEM deposit spots corresponding to all of the M29 runs were re-analyzed by CES's laboratory QuanX XRF analyzer 6 weeks after the initial validation test. In addition, 10 XCEM filter deposit spots were analyzed over a 2-month period to evaluate Hg stability. Spectra from these tests were compared with 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 CVAA 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 (Butte, MT).

Results and Discussion

The Hg results for the original validation test are summarized in Table D1. There is a clear bias of about 26 percent between the XCEM results and the M29 results. Normally, the M29 results would be accepted as the best estimate of stack Hg concentration and it would be assumed that the candidate method (XCEM) was in error. However, because of the total QA associated with the XCEM and the fact that the XRF analysis is nondestructive, 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 D1. Mercury reported concentrations during Year 2002 M29 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**

Loss of mercury from the XCEM filter

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 Hg (see Table 31 in main body of text).

A series of 10 spots on the XCEM filter tape were reanalyzed between 21 June 2002 and 11 July 2002. The spots, which represent 10 XCEM runs, showed a consistent Hg loss of about 30 percent over the 3-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.

XCEM measurements (XCEM). To confirm this loss of Hg, 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 2 months earlier. The X-ray spectra from the original analysis of XCEM runs 939 to 943 (M29 run 4) are compared in Figure D1. This comparison clearly shows that agreement is good for the two closest analyte peaks for Zn and Pb, but reduction is substantial in the peak intensity for the Hg L-alpha analyte line. A comparison of the XCEM Hg concentrations measured during the M29 testing (14 May 2002) with those measured with the XCEM on 25 July 2002 indicate a 31.4 ± 0.4 µg/m^3 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

R5-2014-0104710000365

Zn and Pb as well as the ratio of Hg to these elements. The reduction in Hg to Zn ratio, for example, was 29.1 percent, which is in good agreement with the Hg-measured reduction.

Clearly, Hg 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 suggest that a substantial portion of the M29 Hg was also lost from the M29 PM filter deposits prior to analysis.

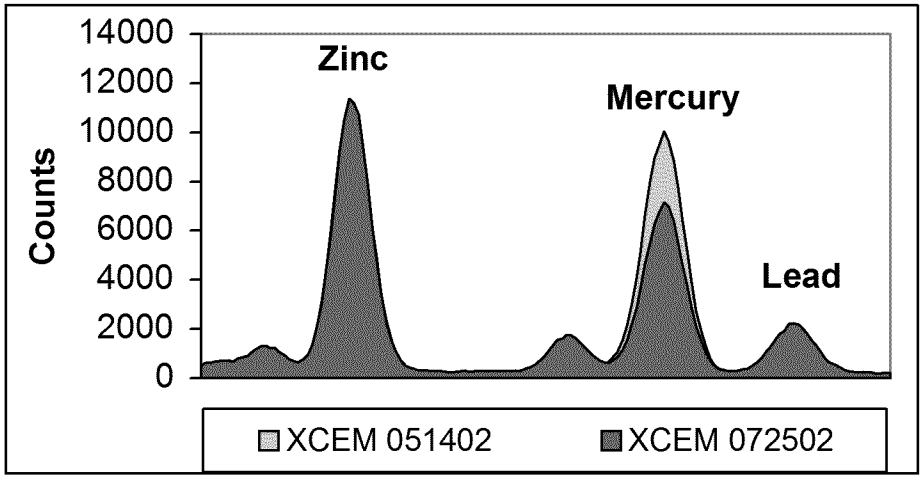

Figure D1. Comparison of XCEM x-ray spectra measured during M29 testing and 71 days later.

Instability of M29 Hg PM deposit highly likely

Although there is no direct evidence of the loss of Hg 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.

Train location of Hg 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 D2. It is interesting to note that, during the 2001 testing, only about 1 percent of the Hg was deposited on the quartz fiber filter. This is typical of most stack measurements of Hg, so there is little concern for the stability of the PM deposited on the filter. This is not the case, however, for the 2002 Hg measurements. During these latter tests, 18 percent of the Hg was deposited on the filter during runs 1 through 5, with no Pb in the Hg-Ni-Zn spiking solution. After adding Pb to the spiking solution, the percent of Hg depositing on the filter increased to 29 percent for the remaining M29 runs.

Table D2. Comparison of the location in M29 sampling trains where the Hg 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 Hg concentrations were 12 percent greater than the predicted concentrations; similar to the 18 percent (12 percent with corrected solution concentrations) measured in 2002 with the XCEM. On the other hand, the 2002 M29 results are 6 percent less than the predicted concentrations rather than 12 percent greater as in 2001.

These results are certainly consistent with the hypothesis that M29 Hg results are low because there was a loss of Hg 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 Hg compounds and amalgams of Hg are relatively unstable and have relatively high vapor pressures. Thus, it should not be surprising that if there is a substantial portion of the Hg 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.

Correlation with percent Hg on M29 filter. The percent difference between the M29 Hg results and the XCEM results is significantly correlated with the percent Hg on the M29 filters as is illustrated in Figure D2. That is, the percent difference between the two methods (percent loss from the M29 filter) is dependent on the fraction of the total Hg 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 Hg from the M29 filter.

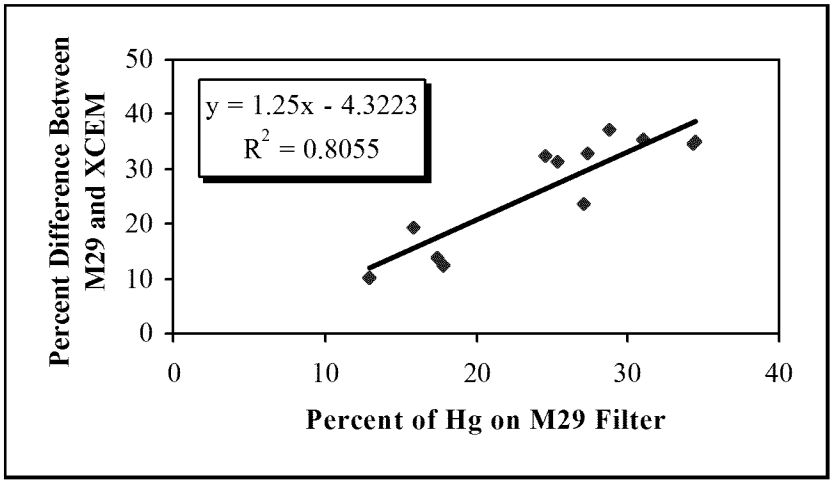

Figure D2. Percent difference between M29 and the XCEM vs. percent of Hg on the M29 filter.

Precision

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

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 Hg. Thus, the ratio of Hg should not vary significantly since the concentrations for these two elements was kept constant for these latest tests. The XCEM measured Hg to Ni ratio was 1.37 ± 0.015 (1.1 percent relative) and close to both the M29 ratio, 1.41 ± 0.116 (8.3 percent 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.

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 Hg concentrations at the time of extrac-

R5-2014-0104710000365

tion would be about 10 percent lower than measured by the CES XRF analyzer. The observed difference was 14 percent.

Conclusion

The weight of evidence clearly indicates that the XCEM Hg deposit was unstable as was the M29 PM deposit on the quartz fiber filter. This instability most likely caused the difference between the Hg 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 PS-10 RA 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.

R5-2014-0104710000365

Abbreviations and Acronyms

AEC	Army Environmental Center
AED	Ammunition Equipment Directorate
AMP	Alternative Monitoring Plan
AMS	Advanced Monitoring Systems (Center)
APE	ammunition peculiar equipment
CAAA	Clean Air Act Amendments (of 1990)
CEM	continuous emission monitor
CERL	Construction Engineering Research Laboratory
CES	Cooper Environmental Services
CHPPM	U.S. Army Center for Health Promotion and Preventive Medicine
CVAA	cold vapor atomic absorption
EPA	U.S. Environmental Protection Agency
EQT	Environmental Quality Technology
ERDC	U.S. Army Engineer Research and Development Center
ETV	Environmental Technology Verification (program)
HAP	Hazardous Air Pollutants
HWC	hazardous waste combustors
ICP	inductively coupled plasma
LIBS	laser-induced breakdown spectroscopy
LVM	low volatile metals
MACT	Maximum Achievable Control Technology
M17	EPA Reference Method 17
M29	EPA Reference Method 29
MF	membrane filter
NESHAP	National Emissions Standard for Hazardous Air Pollutants
NIST	National Institute of Standards and Technology
PM	particulate matter
PS-10	EPA Proposed Performance Specification 10
QA/QC	quality assurance/quality control

R5-2014-0104710000365

QFF	quartz fiber filter
QSIS	Quantitative Spike Injection System
RA	relative accuracy
RCRA	Resource Conservation and Recovery Act
RIF	resin-impregnated filter
RSD	relative standard deviation
SCFM	standard cubic feet per minute
TEAD	Tooele Army Depot
XCEM	XRF-based continuous emission monitor
XRF	x-ray fluorescence

Chemical elements

Ag	silver	Pb	lead
As	arsenic	Pd	palladium
Ba	barium	Sb	antimony
Be	beryllium	Se	selenium
Cd	cadmium	Sn	tin
Cr	chromium	Tl	thallium
Hg	mercury	Zn	zinc
Ni	nickel		

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14. ABSTRACT

Army demilitarization incinerators will need to comply with the Hazardous Waste Combustor National Emission Standard for Hazardous Air Pollutants that will regulate metals and metal compounds listed under the Clean Air Act Amendments. A large problem for these incinerator operations is limited knowledge of the type and quantity of emitted metals, so that compliance may be determined only through trial burn emission tests. A continuous emission monitor (CEM) for multi-metals will provide the emission data, a tool to help meet compliance requirements, and the opportunity to adjust burn strategies for increased production. A user-friendly multi-metal CEM that uses x-ray fluorescence (XRF) as the analytical method and an automated sampling system that provides extractive batch sampling onto a filter tape (XCEM) was demonstrated at the 1236 Deactivation Furnace at Tooele Army Depot, Utah. The unit was compared to EPA Reference Method 29 during two separate tests (2001 and 2002). The second test was performed after improvements were made to the sample transport and system calibrations. The results indicate that the XCEM has met the proposed Performance Specification 10 for multi-metal CEMs except for some of the relative accuracy requirements. Its failures are attributed to inadequacies in the reference method. The monitor is proving useful at Tooele and is ready for implementation at other Army demilitarization incinerators.

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