

US EPA ARCHIVE DOCUMENT

Environmental Technology Verification Report

COOPER ENVIRONMENTAL SERVICES
XCEM
MULTI-METALS CONTINUOUS EMISSION
MONITOR

Prepared by



Battelle

Under a cooperative agreement with



ETV ✓ ETV ✓ ETV ✓

May 2002

Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

Cooper Environmental Services
XCEM

Multi-Metals Continuous Emission Monitor

by

Jeffrey Myers
Thomas Kelly
Charles Lawrie
Karen Riggs

Battelle
Columbus, Ohio 43201

Notice

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development, has financially supported and collaborated in the extramural program described here. This document has been peer reviewed by the Agency and recommended for public release. Mention of trade names or commercial products does not constitute endorsement or recommendation by the EPA for use.

Foreword

The U.S. EPA is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permittees, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of six environmental technology centers. Information about each of these centers can be found on the Internet at <http://www.epa.gov/etv/>.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. In 1997, through a competitive cooperative agreement, Battelle was awarded EPA funding and support to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/07/07_main.htm.

Acknowledgments

The authors wish to acknowledge the several agencies and people who contributed to the conduct of this verification. We acknowledge K. James Hay of the U.S. Army Corps of Engineers, Engineer Research and Development Center, Construction Engineering Research Laboratory, for his overall support and direction of the test activities. We also thank Dee Russell and the staff of the conventional munitions deactivation furnace at the Tooele Army Depot for their cooperation and guidance in the verification activities. Reference method sampling and chemical analysis were conducted by the U.S. Army Center for Health Promotion and Preventive Maintenance; operations at the Tooele Army Depot were led by Mike Pattison. Steve Bryson of MSE Technology Applications, Inc., Butte, Montana, directed spiking of metal solutions into the deactivation furnace flue gas.

Contents

Notice	ii
Foreword	iii
Acknowledgments	iv
List of Abbreviations	viii
1. Background	1
2. Technology Description	2
3. Test Design and Procedures	4
3.1 Introduction	4
3.2 Test Facility	4
3.3 Test Schedule	8
3.4 Experimental Design	9
3.5 Data Comparisons	10
3.6 Material and Equipment	12
4. Data Quality	14
4.1 Deviations from the Test/QA Plan	14
4.2 Facility Calibrations	15
4.3 M29 Sampling and Analysis	15
4.3.1 M29 Detection Limits and Blank Results	15
4.3.2 M29 Analytical Duplicates	16
4.3.3 M29 Precision	17
4.4 Audits	17
4.4.1 Technical Systems Audit	17
4.4.2 Performance Evaluation Audits	19
4.4.3 Data Quality Audit	22
5. Statistical Methods	23
5.1 XCEM Concentration	23
5.2 Relative Accuracy	23
5.3 Correlation with Reference Method	24
5.4 Precision	24

5.5 Span, Zero, and Internal Standard Drift 24

5.6 M29 Bias and XCEM Bias Relative to M29 25

6. Test Results 26

 6.1 XCEM Concentration 26

 6.2 Relative Accuracy 31

 6.3 Correlation with Reference Method 34

 6.4 Precision 34

 6.5 Span, Zero, and Internal Standard Drift 36

 6.6 XCEM Bias Relative to M29 38

 6.7 Response Time 38

7. Performance Summary 40

8. References 41

Appendix A. XCEM Data During M29 Runs A-1

Figures

Figure 2-1. XCEM Supplied by CES 2

Figure 2-2. XCEM Housing and Gas Transport System at TEAD 3

Figure 2-3. XCEM Extraction System, Cassette, and Chassis 3

Figure 3-1. Deactivation Incinerator at TEAD Incinerator 5

Figure 3-2. TEAD Incinerator Stack 8

Figure 6-1. XCEM and M29 Data During Verification Test 28

Figure 6-2. Uncorrected XCEM Arsenic Concentrations vs.
XCEM Lead Concentrations 32

Figure 6-3. Correlation Between XCEM and M29 35

Figure 6-4. XCEM Palladium Internal Standard Readings During M29 Testing 38

Tables

Table 3-1. Typical Operating Parameters for the TEAD Incinerator 5

Table 3-2. TEAD Incinerator Metal Emission Limits During Verification Testing 8

Table 3-3. XCEM Test Dates and Associated TEAD Incineration Feedstreams 9

Table 3-4. Tooele Metal Emission Limitations and Target Spiking Levels 10

Table 3-5. Summary of Data to be Obtained During XCEM Verification Test 11

Table 4-1. Estimated Detection Limits for Analysis of Metals by M29 16

Table 4-2. Flue Gas Metals Concentrations Determined by Duplicate M29 Trains
at the TEAD Incinerator 18

Table 4-3. Summary of RPD Results from Duplicate M29 Trains
in XCEM Verification 19

Table 4-4. Summary of PE Audit Results on M29 Sampling Equipment
in XCEM Verification Test 20

Table 4-5. Results of Field Spikes of M29 Trains 21

Table 6-1. Summary of Results from XCEM and M29 for Each Test Run 27

Table 6-2. Relative Accuracy Results for XCEM 32

Table 6-3. Correlation Between XCEM and M29 35

Table 6-4. XCEM Precision 36

Table 6-5. XCEM Span and Zero Readings During Verification Testing 37

Table 6-6. XCEM Bias Relative to M29 39

List of Abbreviations

AMS	Advanced Monitoring Systems
Ag	silver
APE	Ammunition Peculiar Equipment
As	arsenic
As ₂ O ₅	arsenic oxide
Ba	barium
Ba(NO ₃) ₂	barium nitrate
Be	beryllium
BTU/hr	British thermal units per hour
Cd	cadmium
Cd(NO ₃) ₂	cadmium nitrate
CEM	continuous emission monitor
CEMS	continuous emission monitoring systems
CES	Cooper Environmental Services (of Beaverton, Oregon)
CHPPM	Center for Health Promotion and Preventive Medicine, U.S. Army
CO	carbon monoxide
CO ₂	carbon dioxide
Cr	chromium
CrO ₃	chromium trioxide
DLS	Directorate of Laboratory Sciences
dscm	dry standard cubic meter
EPA	United States Environmental Protection Agency
ETV	Environmental Technology Verification program
Hg	mercury
Hg(NO ₃) ₂	mercury (II) nitrate
ID	internal diameter
K ₂ (C ₄ H ₂ O ₆ Sb) ₂	potassium antimony tartrate
mg	milligram
M29	EPA Method 29
M301	EPA Method 301
ml	milliliter
MSE-TA	MSE Technology Applications Inc. (of Butte, Montana)
Ni	nickel
Ni(NO ₃) ₂	nickel nitrate
O ₂	oxygen
Pb	lead
Pd	palladium
PE	performance evaluation
PLC	programmable logic circuit
ppm	parts per million

PS-10	Performance Standard 10 (EPA's proposed standard for multi-metal CEMS)
QA	quality assurance
QC	quality control
QMP	quality management plan
RA	relative accuracy
RCRA	Resource Conservation and Recovery Act
RPD	relative percent difference
RSD	relative standard deviation
Sb	antimony
scfm	standard cubic feet per minute
Se	selenium
TEAD	Tooele Army Depot
Tl	thallium
TSA	technical systems audit
WFRMS	waste feed rate monitoring system
XCEM	X-ray based continuous emission monitor
XRF	X-ray fluorescence
Zn	zinc
Zn(NO ₃) ₂	zinc nitrate
ZnO	zinc oxide
μg	microgram
μg/m ³	micrograms per cubic meter

Chapter 1 Background

The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized standards and testing organizations; with stakeholder groups that consist of buyers, vendor organizations, and permittees; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of a continuous emission monitor for multiple metals in stack gas. This verification report presents the procedures and results of the verification test for that instrument, the X-ray based continuous emission monitor (XCEM) from Cooper Environmental Services (CES).

Chapter 2 Technology Description

The objective of the ETV AMS Center is to verify the performance characteristics of environmental monitoring technologies for air, water, and soil. This verification report provides results for the verification testing of the XCEM. The following description of the XCEM is based on information provided by the vendor.

The XCEM (Figure 2-1) extracts a sample of stack gas and concentrates the metals of interest on a chemically treated filter tape. Following collection, the filter tape advances, moving the sample spot to an analysis area where a laboratory-grade X-ray fluorescence (XRF) instrument is used to determine metal mass. The system is automated and produces concentration data every 10 to 20 minutes for 19 elements of interest. The XCEM components are divided into three major categories: the extraction system, the sampling and analysis system, and the control system.



Figure 2-1. XCEM Supplied by CES

The XCEM extraction system collects a representative stack gas sample from the stack and transports the sample to the filter tape. For this project, the U.S. Army provided the sample probe and insulated sample line, as well as the enclosure for housing the XCEM (Figure 2-2). The stack gas temperature was monitored where it enters the XCEM enclosure, and testing was conducted only when this temperature was above the dew point for water. Upon entrance into the XCEM housing, the stack gas passes through a heat-traced stilling chamber that expands the tubing diameter and slows the gas velocity (Figure 2-3). An eductor, located downstream of the stilling chamber, is used to pull the stack gas through the extraction system. Of the two to three standard cubic feet per minute (scfm) that pass through the stilling chamber, a sub-sample of approximately 0.8 liter per minute is extracted and directed through a filter tape, concentrating the metals sample for analysis.

Following filtration, the stack gas is subsequently transported to the XCEM chassis where drying and volume determination take place (Figure 2-3). The excess (i.e., unfiltered) stack gas is transported out of the stilling chamber through a flowmeter and is vented or returned to the stack.

The sampling cassette holds a four-week supply of filter tape on a reel-to-reel system that is automated to accurately move the tape from the sampling to the analysis position. Sampling and analysis occur simultaneously, resulting in a continuous monitoring system that produces metal concentration values every 10 to 20 minutes. 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 control (QC) 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 filtrate on the tape can be reanalyzed at a later date if the end-user requires additional data.

The XCEM is controlled by a personal computer using a custom WonderWare⁽¹⁾ software interface. All day-to-day functions of the XCEM have been 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 be imported into Excel or an equivalent program for subsequent analysis. Flows, temperatures, concentrations, and pressure are logged in real time on the screen computer monitor.



Figure 2-2. XCEM Housing and Gas Transport System at TEAD

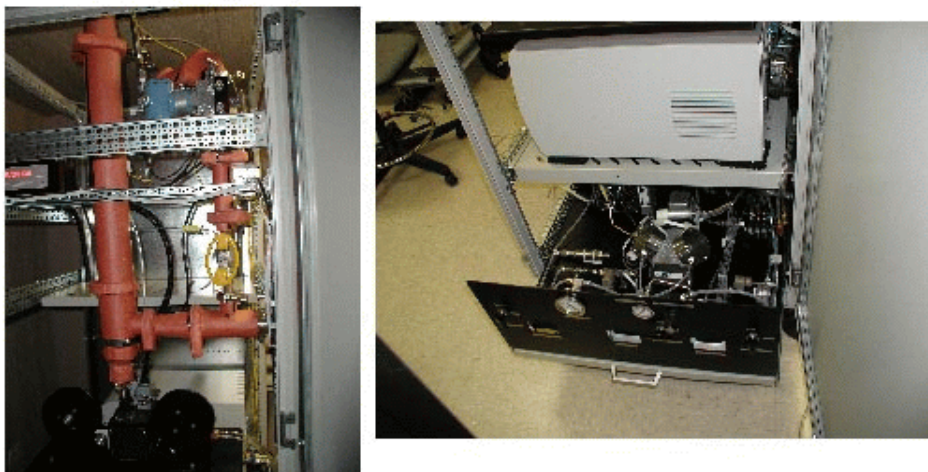


Figure 2-3. XCEM Extraction System, Cassette, and Chassis

Chapter 3

Test Design and Procedures

3.1 Introduction

This verification test was conducted according to procedures specified in the ETV *Test/QA Plan for Pilot-Scale Verification of Continuous Emission Monitors for Multi-Metals*.⁽²⁾ The overall objective of the verification test was to provide quantitative evaluation of the performance of the XCEM under real-world conditions. The test activities provided data for verification of the following performance parameters of the XCEM:

- Relative accuracy
- Correlation with reference method
- Precision
- Span, zero, and internal standard drift
- Bias
- Response time.

Relative accuracy, correlation with the reference method, and precision (i.e., repeatability at stable test conditions) were assessed for all of the elements being measured by the XCEM. The reference method in the assessment of relative accuracy and correlation was EPA Method 29⁽³⁾ (M29). Precision was assessed in terms of the variability of XCEM response during periods when the stack gas flow rate and volume and the isokinetic rate were stable. The XCEM has an automated check for drift that measures a Pd internal standard with each XCEM test run. Drift also was checked by daily XCEM span and zero QA measurements. Bias was identified using EPA Method 301⁽⁴⁾ (M301) protocols. Response time was determined as the time between the start of one sampling period and the beginning of a second sampling period.

3.2 Test Facility

Verification testing took place at the U.S. Army's Tooele Army Depot (TEAD) in Tooele, Utah, TEAD Building 1320 deactivation incinerator (APE-1236M1) (Figure 3-1). This section describes the TEAD incinerator and the procedures for operating it for this test. The TEAD incinerator is currently regulated under the Resource Conservation and Recovery Act (RCRA) for antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), silver (Ag), and thallium (Tl). Of the twelve regulated elements, five are typically found in the feedstream—Sb, Ba, Cd, Cr, and Pb, whereas only Pb is typically found in the stack gas. The XCEM was tested for its ability to measure the



Figure 3-1. Deactivation Incinerator at TEAD

five elements found in the feed-stream, as well as As, Hg, Ni, and a nonregulated metal, zinc (Zn). Except for Pb, the stack gas levels of these target metals were prepared by spiking metal solutions into the stack gas at the base of the stack.⁽⁵⁾ These elements were selected to challenge the XCEM over a large range of analysis conditions and elemental concentrations.

The TEAD incinerator, which runs on diesel fuel, is designed to incinerate decommissioned conventional 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%. Typical stack particulate matter concentrations are in the 10 milligram per dry standard cubic meter (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 with preset operating standards. The incinerator consists of a main control panel, continuous emission monitoring systems (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. These components of the incinerator are described below.

Table 3-1. Typical Operating Parameters for the TEAD Incinerator

Parameter	Typical Value
Afterburner Temp. (°F)	1,630
Baghouse ΔP (in. H ₂ O)	4
Baghouse Inlet Temp. (°F)	860
Kiln Feed End Draft Pressure (in. H ₂ O)	-0.2
Kiln Feed End Temp. (°F)	375
Kiln Burner End Temp. (°F)	1,000
O ₂ – CEM (%)	15
CO (ppm)	8
Stack Temp. (°F)	500
Stack Gas Velocity (ft/sec)	46

-
- **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 programmable logic circuit (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 that provides centralized and integrated data management, process graphics, operator interface, and report generation.
 - **CEMS.** CEMS are in place to measure carbon monoxide (CO) and oxygen (O₂) in the exhaust stack. The CEMS include a sample extraction probe, heat-traced sampling lines, calibration ports, a refrigerated condenser, a sample pump, filters, and flow meters. The sample extraction port is located in the exhaust stack approximately 20 feet above grade. The CEMS include automatic calibration, which allows the monitors to be calibrated periodically without operator intervention.
 - **WFRMS.** 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.
 - **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. However, for safety reasons, 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.
 - **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 countercurrent to the movement of the ammunition through the rotary furnace. Combustion gases and entrained ash exit the furnace adjacent to the feed chute. Nonentrained 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-foot-long, 30.5-inch-diameter retort toward the burner end by spiral flights. As the ammunition approaches the flame, it either detonates or burns 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 rotary furnace is equipped with a Hauck 783 proportioning burner located at the discharge end. The burner has a capacity of 3 million British thermal units per hour (BTU/hr) and a nominal turndown ratio of 4:1. The feed end temperature of the

furnace ranges between 350 to 450°F, while the discharge end ranges from 800 to 1,100°F during normal operation. The rotary furnace is operated under a slight negative pressure.

- **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.
- **Cyclone.** Large particles are removed from the gas stream by the cyclone. The cyclone has a 90 to 95% removal efficiency for particles 10 microns and larger. The cyclone rotates clockwise, with inlet and outlet ducts at 90° separation. Collected material is removed from the cyclone at the bottom by a double tipping valve. The valve has two gates that are motor driven. The gates open alternately so that only one gate is open at any time, thus maintaining the negative pressure.
- **Afterburner.** The afterburner is built 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 4,000 scfm of flue gas from 350 to 450°F to over 1,600°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.
- **Discharge Conveyor.** The solid waste exits the furnace by the discharge conveyor located at the discharge/burner end. The solid waste is typically composed of 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.
- **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 by JT Systems Incorporated. The flue gases from the afterburner are transported to the baghouse by 120 feet of 30-inch-diameter stainless steel ducting. The ducting is long enough to produce a temperature drop from 1,600°F at the exit of the afterburner to less than 1,000°F entering the baghouse. The baghouse contains 154 cerafil ceramic candles that are 5.75 inches in diameter and 10 feet long. This results in a total filter area of 2,330 square feet with a filtration velocity of 4.97 feet per second. The baghouse operates with a delta pressure range of 0.5 to 6.0 inches of water column. Collected material settles into the hopper below and is exhausted through a double tipping gate valve into a sealed 55-gallon drum while maintaining an air seal on the baghouse assembly.

- **High-Temperature Draft Fan.** The gas stream is pulled through the baghouse by an induced draft fan. The fan is a Fan Equipment Company Model M-21 I.E. The fan is capable of pulling 6,700 actual cubic feet per minute at a draft (negative pressure) of 30 inches of water column.
- **Exhaust Stack.** The A36 carbon steel, circular exhaust stack is approximately 30 feet high (34 feet with extension) and has a nominal ID of 20 inches (Figure 3-2).



Figure 3-2. TEAD Incinerator Stack

For the verification test, metals in the TEAD incinerator stack gas were regulated under a temporary authorization permit. The hourly emission limits for each regulated metal are shown in Table 3-2. Of the 12 regulated metals, five 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. Consequently, the other metals were introduced by spiking metals solutions into the stack.

Table 3-2. TEAD Incinerator 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)	2,400	Nickel (Ni)	930
Beryllium (Be)	0.20	Selenium (Se)	180
Cadmium (Cd)	0.26	Silver (Ag)	140
Chromium (Cr)	0.04	Thallium (Tl)	14

3.3 Test Schedule

Setup for the XCEM verification test took place at the TEAD incinerator during the week of May 7, 2001. The XCEM verification test occurred over a four-day period on May 14, 15, 16, and 17, 2001. A total of 13 M29 runs were conducted, for two hours each, consisting of three

runs on May 14, four runs on May 15, four runs on May 16, and two runs on May 17. All nine metals of interest were tested during each run; however, lower concentrations of Hg, Ni, Sb, and Zn were spiked into the stack gas during the last six runs.

3.4 Experimental Design

Both the kiln and afterburner were fired with diesel fuel for all 13 test runs. Table 3-3 shows the incinerator feedstreams for the 13 M29 runs. During M29 Runs 1 and 2, M17 .50-caliber bullets were incinerated. However, during these runs, the XCEM observed excessively high lead concentrations, which were traced to a problem in the bypass damper valve in the incinerator baghouse. This led to a decision not to incinerate additional ammunition during the test until repairs to the bypass valve could be made. For this reason, no ammunition was burned during test Runs 3 through 11. Following the bypass repair, two final M29 runs were conducted while incinerating Mark 344 fuses. Table 3-4 shows the emission limits and target spiking concentrations for the nine elements that were measured by the XCEM during all 13 of the verification test runs. In all test runs, eight of these metals were spiked directly into the stack upstream of the XCEM and M29 sampling locations.⁽⁵⁾ These metals were spiked at the level shown in Table 3-4. Pb, however, was not spiked since the incinerated munitions provide measurable concentrations of lead without spiking. Note that, for Hg, Ni, Sb, and Zn, different spike levels were used in Runs 1-7 than in Runs 8-13.

Table 3-3. XCEM Test Dates and Associated TEAD Incineration Feedstreams

May 14			May 15				May 16			May 17		
Run	Run	Run	Run	Run	Run	Run	Run	Run	Run	Run	Run	Run
1	2	3	4	5	6	7	8	9	10	11	12	13
M17	M17	No	No	No	No	No	No	No	No	No	Mark	Mark
.50	.50	Ammo	Ammo	Ammo	Ammo	Ammo	Ammo	Ammo	Ammo	Ammo	344	344
caliber	caliber										Fuses	Fuses

Three separate solutions were prepared for the spike injections.⁽⁵⁾ The first solution contained arsenic oxide (As_2O_5), cadmium metal, and chromium trioxide (CrO_3), dissolved in a dilute nitric acid solution. The second solution contained mercury (II) nitrate ($Hg(NO_3)_2$), nickel nitrate ($Ni(NO_3)_2$), and zinc oxide (ZnO), dissolved in dilute nitric acid. The final solution contained potassium antimony tartrate ($K_2(C_4H_2O_6Sb)_2$) and barium nitrate ($Ba(NO_3)_2$), dissolved in water.⁽⁵⁾ Spiking was conducted by MSE Technology Applications Inc. (MSE-TA), using three atomizers to inject solutions containing the metals of interest directly into the base of the stack. Manufacturer specifications for the atomizers establish droplet size distributions based on pressure and airflow space 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 mass was calculated to be in the one to four micron range. M29 results⁽⁶⁾ showed that 10 to 15% of the spiked metal mass was collected in the sampling probe of the M29 train. This result is typical for M29 sampling at an incinerator and may indicate that the spiked metal particle size range was similar to other incinerators. Spiking of metals solutions continued at a constant rate throughout

Table 3-4. Tooele Metal Emission Limitations and Target Spiking Levels

	Emission Limits ^a (µg/dscm)	Target Spiking Level ^a (µg/dscm)	
		M29 Runs 1-7	M29 Runs 8-13
As	25	14	14
Ba	540,000	200	200
Cd	58	34	34
Cr	10	5	5
Hg	3,145	280	88
Ni	209,000	460	180
Pb	966	NS	NS
Sb	3,145	520	200
Zn	NR	460	180

^a The concentration in µg/dscm assumes a stack flow rate of about 4,474 dscm/hr.

NR = not regulated

NS = not spiked

each test day, to assure constant flue gas metals content. That is, the spiking process was continuous, and was not turned on and off, e.g., to coincide with M29 sampling intervals. Additional information on the spiking procedures and results can be found in the MSE-TA report to the U.S. Army Corps of Engineers.⁽⁵⁾

Stack gas metal concentrations were simultaneously determined by the XCEM and two M29 sampling trains. The M29 trains sampled for two hours, while XCEM data, which are recorded every 20 minutes, were averaged for the M29 test run. A total of 13 dual M29 test runs were performed by the U.S. Army Center for Health Promotion and Preventive Medicine (CHPPM) Air Quality Surveillance Program.⁽⁶⁾ In all cases, when reference method data were being taken, the spiking of the indicated metals was held constant throughout the entire sampling period.⁽⁵⁾ The intent of this approach was to allow comparisons of XCEM data with reference method data under constant conditions. CHPPM’s Directorate of Laboratory Sciences (DLS) conducted laboratory analysis of the sampling trains.⁽⁶⁾

Sample handling, analysis, and all associated QA/QC activities conformed to the requirements of M29.⁽⁶⁾ Accuracy data for metal analysis were confirmed with two field spikes of the nine measured metals into blank sampling trains. Media blanks of the M29 solutions and filter were also analyzed. Sample integrity was maintained using chain of custody and a designated sample custodian. Unique sample identification numbers were implemented so that final data used for verification could be traced back through the analytical process to the original sample. Data quality results for the M29 reference data are presented in Section 4.3.

3.5 Data Comparisons

This section describes how the reference and CEM data were used and compared to quantify the performance of the XCEM. Table 3-5 summarizes the data used for the verification comparisons.

Table 3-5. Summary of Data to be Obtained During XCEM Verification Test

Performance Parameter	Objective	Comparison Based On	No. of Data Points^a
Accuracy	Determine degree of quantitative agreement with reference method	Reference method results	13
Correlation	Determine degree of correlation with reference method	Reference method results	13
Precision	Determine XCEM precision during periods when stack and spiking conditions are held constant	XCEM readings during constant operating and spiking conditions	6 per run
Span and Zero Drift	Determine XCEM response to calibration and blank samples	XCEM automated daily QA routine	4
Internal Standard Drift	Determine XCEM ability to measure consistently over the course of the test	Determine variation in palladium concentrations determined with each XCEM measurement	6 per run
Bias	Determine if inter-method bias exists between M29 and the XCEM	Reference method results	13
Response Time	Determine XCEM response time as a batch CEM	XCEM cycle time in continuous monitoring of metal concentrations	6 per run

^aNumber of data points used in the verification for each target metal.

Relative accuracy was verified by comparing the CEM results against the M29 results for each metal. The total train results were combined for the relative accuracy calculations. Precision of the dual M29 sampling trains for each run was determined by a comparison of the dual M29 sample runs using an M301 approach. M29 results that were identified as outliers were reported, but were not used for verification. The intent of this approach was 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 was 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 was suggested, an effort was made to find an assignable cause for the divergent result. For valid test runs, M29 concentrations were averaged and compared with reported XCEM data.

Correlation of the XCEM with M29 was verified using the same data used to assess relative accuracy. Correlation was calculated for each metal measured by the XCEM.

Precision of the XCEM was established based on the successive XCEM readings during the M29 runs, when spike injections and incinerator conditions were stable. The percent relative standard deviation (RSD) of the successive readings was determined for each metal within each M29 run, as an indication of the precision of the XCEM.

Span and zero determinations also were conducted daily by the XCEM. The automated XCEM span routine extended a plunger containing four of the metals of interest (Cd, Cr, Hg, and Pb) into the analysis area. The plunger was analyzed by the XCEM in the same manner as for a sample spot on the tape. Zero readings were determined by analysis of blank filter tape. The variation in span and zero readings was determined as an indicator of instrument drift. Internal

standard drift also was determined by evaluation of XCEM-reported palladium concentrations. As part of the XCEM QA program, a palladium rod was permanently fixed above the X-ray beam and below the filter tape. The palladium rod was measured with each sample and a running record of the reported Pd concentrations was maintained. The %RSD for palladium concentrations indicated the XCEM internal standard drift during testing.

Bias was determined relative to the M29 sample results using M301. First, M29 sample trains were compared with each other to determine any significant bias. M29 data sets that did not show significant intra-method bias were averaged, and the average results were compared with the XCEM reported concentrations.

The XCEM sampled for 10 to 20 minutes, depending upon the desired detection limits. Within a few seconds of sampling, the exposed tape was moved into the XRF analysis region. Analysis required the same amount of time as sampling. Following analysis, concentrations were determined and recorded in a fraction of a second. For these tests, the response time was 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 was equivalent to the analysis time.

Setup and maintenance needs were documented qualitatively, both through observation and through communication with the CEM vendor during the test. Factors noted included the frequency of scheduled maintenance activities, the downtime of the CEM, and the number of staff operating or maintaining it during the verification test.

3.6 Material and Equipment

The XCEM requires about 10 scfm of dry compressed gas (e.g., air or nitrogen) to provide a vacuum in the extraction system. A small amount of purified compressed gas also is used to drive the XCEM pneumatics. The atomizers used for spiking required about 10 scfm of dry air. The spike injection solutions included $\text{Ba}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, $\text{Cr}(\text{NO}_3)_3$, As_2O_5 , $\text{Hg}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, and $\text{Sb}(\text{NO}_3)_3$. Solutions were prepared on-site to allow for flexibility in responding to background metal concentrations found in the TEAD incinerator.

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

CHPPM provided laboratory equipment for sample recovery and analysis. This included all chemicals and solutions for rinsing train components and recovering impinger samples, as well as cold vapor atomic absorption or atomic fluorescence spectroscopy equipment for mercury determination at the DLS.

The verification also made use of monitoring equipment already integrated into the TEAD facility. This equipment included monitors for major flue gas constituents [O_2 , carbon dioxide

(CO₂), as well as sensors for temperature and pressure. These devices were considered part of the TEAD facility for purposes of this test and were operated during this verification according to normal TEAD procedures.

Chapter 4 Data Quality

4.1 Deviations from the Test/QA Plan

The quality of the verification data was assured by QA/QC procedures, performed in accordance with the quality management plan (QMP) for the AMS Center⁽⁷⁾ and the test/QA plan⁽²⁾ for this verification test. Deviations from the test/QA plan were documented in the verification records during testing at the TEAD facility. Deviations required the approval of Battelle's AMS Center Manager. The following deviations were documented and approved:

- The higher concentration metal injection solutions were used first, and then the lower concentration solutions, which is opposite to the order stated in the test/QA plan. This was done at the request of CES staff to provide the stronger signal to assess XCEM operation at the start of the verification test.
- Ba was spiked to produce a level of 200 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) in the flue gas, rather than 1,000 $\mu\text{g}/\text{m}^3$, as stated in the test/QA plan. This change was planned before the testing began, but was inadvertently not corrected in the test/QA plan.
- Four M29 sampling runs per day were performed on May 15 and 16, instead of three runs per day, as stated in the test/QA plan. This change was made necessary by delays in the start of the verification test.
- Thirteen M29 runs were performed, instead of 12, as stated in the test/QA plan. The 13 runs were performed as follows: three on May 14, four on May 15, four on May 16, and two on May 17. The 13th M29 run was added to ensure that six runs were completed with the low concentration spiking solutions, as planned (the first seven runs having been completed with the high concentration spiking solutions).
- The test/QA plan states that Mark 344 fuses would be the feedstream for the TEAD incinerator throughout verification of the XCEM. Because of a shortage of such fuses, and subsequent problems with the incinerator baghouse, the Mark 344 fuses were used only for the last two M29 test runs (Runs 12 and 13). M17 .50 caliber ammunition was fed into the incinerator for the first two test runs (Runs 1 and 2), and no ammunition was fed during Runs 3 through 11.
- The test/QA plan states that both ammunition feed to the incinerator and the injection of metals spiking solutions would take place throughout all M29 runs. However, as noted above, ammunition was fed to the incinerator only during Runs 1, 2, 12, and 13, with the

result that, in Runs 3 through 11, only the injected metals were present in the flue gas. This procedure was made necessary by the failure of a damper valve in the incinerator baghouse that would have resulted in exceeding the facility's emission permit for lead if ammunition were fed into the incinerator.

None of these deviations had any significant effect on the quality of the verification data.

4.2 Facility Calibrations

This verification made use of monitoring equipment already integrated into the TEAD facility, including CEMs for O₂ and CO₂, as well as sensors for temperature and pressure. These devices were considered part of the TEAD facility and were operated during this verification according to normal TEAD procedures. The CEMS included automatic calibration, which caused the monitors to be calibrated periodically without operator intervention. The results of the facility CEM calibrations were factored into the data on flue gas conditions reported by the facility for this verification.

Flue gas water content was determined from the impinger weights in the M29 trains, by means of an electronic balance located in the M29 train preparation/recovery laboratory at TEAD. That balance was the subject of a performance evaluation (PE) audit, as described in Section 4.4.2.

4.3 M29 Sampling and Analysis

The preparation, sampling, and recovery of samples from the M29 trains followed all aspects of the QA/QC requirements in the method. The CHPPM report on the M29 sampling⁽⁶⁾ includes all field data sheets, M29 equipment calibration procedures and results, and QA/QC results. Stringent sample custody procedures were employed. Samples were either in the direct custody of the sample custodian or under lock and key at all times. Sample custody sheets were included in the M29 data report provided by CHPPM.⁽⁶⁾ Recovered M29 samples were sent for analysis at the CHPPM DLS at Aberdeen Proving Ground, Maryland. All sample analyses were completed within one month after the completion of the field verification test at TEAD.

Because of the importance of the M29 data in this verification, the following sections present key data quality results from the M29 data.

4.3.1 M29 Detection Limits and Blank Results

Any M29 sample fraction showing no detectable concentration of a target metal was assigned a concentration equal to the detection limit for that metal. To make such assignments for nondetect results, the analytical detection limit for each type of sample was estimated by CHPPM staff, based on calibration results and instrument performance criteria.⁽⁶⁾ Table 4-1 lists the detection limits estimated in this way for each target metal, in each of the types of sample fractions recovered from an M29 train. Based on a typical M29 sample volume of 2.1 dscm, the detection

limits in Table 4-1 correspond almost entirely to flue gas levels of about 1 µg/dscm or less, which are negligible in comparison to the actual flue gas levels of the target metals. The only exceptions are for Hg and Zn in the impinger samples (6.0 and 4.8 µg, respectively); but, even for these metals, the equivalent flue gas metal levels of about 2.9 and 2.3 µg/dscm, respectively, are minimal compared with the actual flue gas levels of these metals.

Table 4-1. Estimated Detection Limits for Analysis of Metals by M29

Metal	Filter (µg)	Front-Half Rinse (µg)	Impingers/Back- Half Rinse^a (µg)	Fractions 3A, 3B, 3C^{a,b} (µg)
As	0.50	0.20	0.96	n/a
Ba	2.50	1.00	1.20	n/a
Cd	0.50	0.20	0.48	n/a
Cr	2.50	1.00	0.96	n/a
Hg	0.20	0.20	6.00 ^c	2.20
Ni	2.50	1.00	1.20	n/a
Pb	0.50	0.20	1.20	n/a
Sb	0.50	0.28	0.48	n/a
Zn	2.50	1.00	4.80	n/a

^a Values are approximate due to varying sample volumes.

^b Combined.

^c Elevated due to a required 1:100 dilution (because of high Hg values).

n/a = not applicable.

One blank M29 train was prepared and recovered along with the sample trains to establish the blank levels of the target metals in the various sampling media. No detectable level of As, Cd, Cr, Hg, Pb, or Ni was found on the M29 filter or in any of the impinger sample fractions from the blank train. Detectable levels of Ba and Sb were found only in the filter blank (8.1 µg and 1.14 µg, respectively). This Ba blank level corresponds to about 2% or less of the mass of Ba found on the filters from the 13 M29 sample runs, and this Sb blank level corresponds to about 0.2% or less of the mass of Sb found on those filters. Detectable blank levels of Zn were found only on the filter (6.0 µg) and in the probe rinse (3.4 µg). These combined blank levels for Zn correspond to about 2.5% or less of the combined mass of Zn found in the filter and probe rinse samples from the 13 M29 sample runs. All results were blank corrected.

4.3.2 M29 Analytical Duplicates

A total of 206 duplicate analyses for individual metals in M29 sample fractions were reported by CHPPM, from over three weeks of sample analysis.⁽⁶⁾ These 206 analytical duplicates were obtained by injecting the same sample twice and analyzing each sample for the element of

interest. For only one of those results (a sample containing an extremely high Pb level) did the second analysis differ from the first by over 10%. Furthermore, for only 27 of those results did the second analysis differ from the first by more than 5%. These results indicate excellent precision of the M29 analytical results.

4.3.3 M29 Precision

The results of the M29 sampling at the TEAD incinerator are shown in Table 4-2. Shown are the flue gas concentrations of each target metal determined by each of the duplicate M29 trains (designated as Trains A and B) in each of the 13 M29 runs. Inspection of the data shows that, in nearly all cases, the duplication of results for all metals was good. To determine whether any bias existed between the paired M29 trains, the M301 procedure described in Section 5.6 of this report was used. In addition, reproducibility was assessed by calculating the relative percent difference (RPD) between the two paired trains for each metal in each M29 run. RPD is defined as the difference between the paired M29 results divided by their mean, with the result expressed as a percentage.

Using the M301 procedure, it was determined that there was no statistically significant bias between the paired M29 sampling trains for As, Ba, Cd, Cr, Hg, and Pb. A small but significant bias (i.e., about 6%) was found for Ni, Sb, and Zn, with Train B results slightly higher than Train A results when averaged over all 13 runs.

The results of the RPD calculations are summarized in Table 4-3, which lists for each target metal the average, maximum, and minimum RPD value found from the 13 sets of duplicate M29 results. The average RPD results for all the metals were 8.4% or less, and the average over all M29 runs and all metals was 5.8%. These RPD results indicate close agreement between the duplicate M29 trains, even for Ni, Sb, and Zn, which were identified as having a significant bias by the M301 calculation.

Based on these evaluations of the precision of the duplicate M29 trains, no obvious outliers were identified in the M29 data. Consequently, no M29 data were excluded; and, for each M29 run, the average value of each metal calculated from the duplicate train results was used as the reference concentration for verification of the XCEM.

4.4 Audits

4.4.1 Technical Systems Audit

Battelle's Quality Manager performed an internal technical systems audit (TSA) of the verification test, beginning on May 16, 2001, during testing at the TEAD incinerator. The TSA ensures that the verification test is conducted according to the test/QA plan⁽²⁾ and that all activities associated with the test are in compliance with the AMS Center QMP.⁽⁷⁾ On May 16, the Battelle Quality Manager visited the TEAD incinerator test site, toured the test area, and observed the performance of XCEM monitoring, M29 sampling, and the introduction of metal spike solutions by MSE-TA staff. In this visit, the Quality Manager met with staff from CES,

Table 4-2. Flue Gas Metal Concentrations Determined by Duplicate M29 Trains at the TEAD Incinerator ($\mu\text{g}/\text{m}^3$)

Run No.	As		Ba		Cd		Cr		Hg		Ni		Pb		Sb		Zn	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
1	11.3	10.3	249	264	30.1	30.7	4.4	4.1	295	290	390	380	1463	1773	555	575	447	487
2	11.1	11.0	320	276	39.9	36.3	4.4	4.2	272	280	401	402	3248	3236	625	634	469	473
3	9.3	9.5	196	206	29.6	29.5	4.4	4.1	290	282	375	378	88.0	79.0	539	532	429	407
4	11.9	12.2	247	263	32.1	34.9	6.1	7.9	323	314	439	464	65.4	62.1	629	656	491	500
5	11.3	12.4	226	255	33.5	35.7	5.8	6.7	320	316	395	440	44.8	46.3	593	661	433	475
6	12.0	12.0	260	283	35.0	34.7	6.1	6.1	318	320	469	477	46.0	43.5	663	725	499	524
7	12.0	11.6	268	290	33.8	34.8	6.3	6.5	317	319	472	500	51.5	52.1	680	745	520	559
8	11.6	11.5	257	266	34.3	36.2	6.4	6.6	106	102	197	215	184	212	257	287	209	230
9	11.7	11.0	215	232	34.2	35.2	7.1	6.3	105	105	185	170	80.1	74.8	241	234	199	186
10	11.4	11.4	220	207	33.1	34.8	5.9	6.2	99.8	102	170	153	85.3	83.2	227	216	180	171
11	11.2	11.7	229	237	32.0	33.7	5.8	6.1	101	101	177	195	54.0	54.6	242	269	187	214
12	9.5	9.0	229	199	28.9	26.7	5.1	4.7	108	108	170	153	197	177	241	230	192	170
13	11.9	12.1	231	266	36.0	36.5	6.1	6.2	83.9	83.2	148	165	108	110	265	306	166	181

Table 4-3. Summary of RPD Results from Duplicate M29 Trains in XCEM Verification^a

RPD	RPD Results (%) for Target Metals									Overall
	As	Ba	Cd	Cr	Hg	Ni	Pb	Sb	Zn	
Average	3.5	8.4	4.5	7.5	1.6	6.7	6.4	6.8	7.2	5.8
Maximum	9.3	14.8	9.4	26.3	3.7	11.0	19.2	14.2	13.3	26.3
Minimum	0.2	3.3	0.2	0.2	0.2	0.2	0.4	1.3	0.8	0.2

^a RPD = $(2(A-B)/(A+B)) \times 100$

TEAD, CHPPM, and MSE-TA, as well as with the Battelle Verification Testing Leader. The Quality Manager reviewed the records of all organizations participating in the verification test and visited the M29 sample recovery lab to observe train preparation, sample recovery, and record keeping procedures carried out by CHPPM staff. At that time, the Quality Manager observed spiking of two M29 trains for performance evaluation audit purposes, as described in Section 4.4.2. The TSA was completed on June 12, 2001, when a representative of the Quality Manager visited the CHPPM laboratory in Aberdeen, Maryland, to observe M29 analysis procedures. All observations from the TSA were documented in a TSA report, which was submitted to EPA Quality Management staff on July 27, 2001. No issues were found in the TSA that could adversely affect the quality of the data from this verification. The records concerning the TSA are stored in the custody of the Battelle Quality Manager.

4.4.2 Performance Evaluation Audits

A series of audits was performed to check the quality of reference measurements made in the verification test.⁽²⁾ These audits were performed by Battelle and carried out with the assistance of CHPPM staff.

Table 4-4 summarizes the results of the PE audits on the two sets of M29 sampling equipment and on the M29 impinger weighing equipment. The audits of the temperature and flow rate measurements of the M29 samplers were conducted on the sampling platform near the top of the stack, by a simultaneous measurement with each M29 train and the audit device. The temperature audit was conducted both at ambient temperature (approx. 58°F) and at elevated temperature (approx. 260°F), by collocating the audit thermocouple and the M29 train thermocouple. The balance used to weigh M29 impingers was audited by weighing certified weights. Table 4-4 shows that the PE results on the M29 flow measurements showed agreement with the audit results within about 2%, and the temperature measurements agreed within 1% in absolute temperature. Impinger weighing showed agreement within 0.18%.

Table 4-4. Summary of PE Audit Results on M29 Sampling Equipment in XCEM Verification Test

Measurement Audited	Date	Audit Method	Observed Agreement (% difference)
Flow Rate	5/15/01	Comparison to independent flow rate measurement	1.3% ^a 2.1% ^b
Temperature (absolute)	5/17/01	Comparison to independent temperature measurement	ambient: 0.1% ^a elevated: 1.0% ^a ambient: 0.1% ^b elevated: 0.3% ^b
Impinger weighing	5/16/01	Weighing certified weights	0.18%

^a Results for Nutech 2010A MST Serial No. 90488 sampling unit.

^b Results for Nutech 2010A MST Serial No. 90495 sampling unit.

Table 4-5 summarizes the PE audit results from spiking samples from two blank M29 trains. This PE audit of the M29 analysis was performed by spiking the target metals onto a blank filter, and into aliquots of the sample solutions, from two blank M29 trains. The six sample fractions from each train that received the metals spikes were

- Particulate filter
- 100 ml of 0.1 N HNO₃
- 200 ml HNO₃/H₂O₂ solution + 100 ml of 0.1 N HNO₃
- 100 ml of 0.1 N HNO₃
- 100 ml KMnO₄ solution + 33 ml H₂O
- 25 ml of 8 N HCl + 475 ml H₂O.

The first three fractions listed above were each spiked with 1 ml of a solution containing 20 µg/ml of eight of the target metals (As, Ba, Cd, Cr, Ni, Pb, Sb, and Zn). Also, all six fractions listed above were spiked with 1 ml of a solution containing 10 µg/ml of Hg. The spiked filters were allowed to dry in the laboratory air before they were sealed for shipment for analysis. Table 4-5 shows the results of analysis of the spiked train samples, in terms of both the mass of metal found in each sample and the corresponding percent recovery values relative to the amount spiked. All spike results were within the target range of 70 to 130% recovery, with the following exceptions:

- Field Spike 1 Filter—Zn. The Zn recovery for the filter was approximately 60%. This may be attributed to a high Zn filter blank value (6.0 µg). If the 6.0 µg blank value were not subtracted from this fraction, the recovery would have been approximately 90%.

Table 4-5. Results of Field Spikes of M29 Trains [Mass Recovered (% Recovery)]

	Filter^a, ug (%)	Fraction 2^a, ug (%)	Fraction 3^a, ug (%)	Fraction 4^b, ug (%)	Fraction 5^b, ug (%)	Fraction 6^b, ug (%)
Field Spike Train 1						
As	15.90 (79.5)	18.10 (90.5)	17.70 (88.5)	--	--	--
Ba	22.30 (111.5)	20.70 (103.5)	21.50 (107.5)	--	--	--
Cd	17.00 (85.0)	17.90 (89.5)	17.60 (88.0)	--	--	--
Cr	17.90 (89.5)	20.10 (100.5)	21.30 (106.5)	--	--	--
Hg	1.80 ^c (18)	ND ^c	8.30 (83.0)	10.10 (101)	ND ^d	18.60 ^d (186)
Ni	15.00 (75.0)	19.40 (97.0)	19.70 (98.5)	--	--	--
Pb	20.90 (104.5)	19.20 (96.0)	21.70 (108.5)	--	--	--
Sb	25.26 (126)	19.40 (97.0)	19.60 (98.0)	--	--	--
Zn	12.10 ³ (60.5)	16.10 (80.5)	19.50 (97.5)	--	--	--
Field Spike Train 2						
As	16.90 (84.5)	18.40 (92.0)	17.60 (88.0)	--	--	--
Ba	23.10 (115.5)	21.10 (105.5)	22.10 (110.5)	--	--	--
Cd	18.20 (91.0)	18.00 (90.0)	18.00 (90.0)	--	--	--
Cr	18.70 (93.5)	20.20 (101)	20.80 (104)	--	--	--
Hg	3.90 ^c (39)	0.26 ^c (2.6)	7.90 (79.0)	10.00 (100)	ND ^d	18.60 ^d (186)
Ni	15.50 (77.5)	19.50 (97.5)	19.40 (97.0)	--	--	--
Pb	23.90 (119.5)	19.40 (97.0)	21.10 (105.5)	--	--	--
Sb	25.06 (125.3)	19.80 (99.0)	20.10 (100.5)	--	--	--
Zn	14.40 (72.0)	16.80 (84.0)	19.60 (98.0)	--	--	--

^a Target value is 20 µg/sample (10 µg/sample for Hg)

^b Only Hg was spiked; target value is 10 µg/sample

^c Did not meet recovery target

^d See text

ND = Non-detect

-
- Field Spikes 1 and 2 Filter—Hg. The Hg recoveries on the filter field spikes were 18 and 39%, respectively. The liquid spike was allowed to dry on the filter over a period of a few hours before sealing the petri dish. It may be that some of the Hg was lost from the filter during drying or sample recovery.
 - Field Spikes 1 and 2, Fraction 2—Hg. The Hg field spike results for this fraction were very low (nondetect and 2.6%, respectively) in both spiked trains. Since a mercury spike should be very stable in the HNO₃ matrix, the only plausible explanation is that this fraction was inadvertently not spiked with the Hg solution (the remaining metals in this fraction all met the target recovery values).
 - Field Spikes 1 and 2, Fractions 5 and 6—Hg. The Hg recoveries for Fraction 5 were nondetects. However, the recovery for Fraction 6 was 186%. As part of the sample preparation procedure, Fraction 5 was filtered to remove MnO₂ precipitate, and it is possible that some or all of the Hg was trapped in the MnO₂ precipitate (and therefore in the filter). This filter was then digested in HCl and combined with Fraction 6. Therefore, it is possible that the Hg spiked in Fraction 5 was transferred to Fraction 6 during sample preparation. The combined mercury recovery for Fractions 5 and 6 was approximately 93% in both sets of field spikes, well within the target range.

4.4.3 Data Quality Audit

Battelle's Quality Manager audited at least 10% of the verification data acquired in the verification test. The Quality Manager traced a representative sample of the data from initial acquisition, through reduction and statistical comparisons, to final reporting.

Chapter 5 Statistical Methods

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

5.1 XCEM Concentration

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

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

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 M29 was assessed by

$$RA = \frac{|\bar{d}| + t_{n-1}^\alpha \frac{S_d}{\sqrt{n}}}{\bar{x}} \times 100\%$$

Where d refers to the difference between corresponding M29 and XCEM results, n is the number of runs, and \bar{x} corresponds to the average M29 result. S_d denotes the sample standard deviation of the differences, while t_{n-1}^α is the t value for the $100(1-\alpha)^{\text{th}}$ percentile of the distribution with

n-1 degrees of freedom. The RA was determined for an α value of 0.025 (i.e., 97.5% confidence level, one-tailed). The RA calculated in this way can be interpreted as an upper confidence bound

$$\frac{|\bar{d}|}{\bar{x}}$$

for the relative bias of the analyzer, i.e., , where the superscript bar indicates the average of the differences of the reference values. RA was calculated separately for each metal measured by the XCEM.

For both As and Pb, the RA also was determined using only Runs 3 through 13 due to the high Pb levels in Runs 1 and 2 and the apparent interference in the As measurement caused by those high Pb levels (see Section 6.2). For these calculations, a t-statistic value of 2.28 was used.

5.3 Correlation with Reference Method

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

5.4 Precision

Precision was calculated in terms of the percent RSD of a series of XCEM measurements made during stable operation of the TEAD, with metals injected at a constant level. This precision result reflects the variability in the stack conditions, spiking rate, and XCEM measurements, i.e., 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 were recorded, and the mean and standard deviation of those recordings were calculated. Precision as percent RSD was determined as:

$$P = \frac{SD}{\bar{X}} \times 100$$

where SD is the standard deviation of the XCEM readings and \bar{x} is the mean of the readings. The same calculation was performed for each metal measured by the XCEM, for each of the 13 M29 runs.

5.5 Span, Zero, and Internal Standard Drift

The XCEM performs automated daily internal span and zero checks and also reports a reading from a palladium internal standard with each sample to check for internal standard drift. Span, zero, and internal standard drift were reported in terms of the mean, relative standard deviation,

and range (maximum and minimum) of the readings obtained from the XCEM. The percent RSD was calculated as

where \bar{x} is the mean, and SD is the standard deviation of the readings of the span, zero, or

$$RSD = \frac{SD}{\bar{X}} \times 100$$

palladium internal standard.

5.6 M29 Bias and XCEM Bias Relative to M29

Bias between the paired M29 sampling trains, and between M29 and the XCEM, was determined using an M301 approach. The results were tested for statistically significant bias by calculating the t-statistic and determining if the mean of the differences between the two sampling trains or methods was significant at the 80% confidence level. The t-statistic was calculated by finding the standard deviation of the differences between the two sampling trains or methods:

$$SD_d = \sqrt{\frac{\sum (d_i - d_m)^2}{(n-1)}}$$

Where:

d_i = the difference between paired sample train values

d_m = mean of the d_i values

n = number of paired samples

The t-statistic was then calculated as follows:

$$t = \frac{d_m}{\left(\frac{SD_d}{\sqrt{n}} \right)}$$

The critical value of the t-statistic was 1.356 for 13 runs (two-tailed test with P=0.20). If the calculated t-value was greater than the critical value, the bias as defined by M301 was statistically significant.

M29 data pairs that were determined to be unbiased relative to each other were averaged and used for comparison with the XCEM. Bias between the XCEM and average M29 data was determined as described above, with d_i being the difference between the average M29 and XCEM data.

Chapter 6 Test Results

It was beyond the scope of this verification test to simulate the aging and exposures that may affect a multi-metals CEM during routine long-term use. This verification test evaluated 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 long-term performance may be different from that observed in the testing described here. However, the XCEM did not exhibit any mechanical problems during the test, completing more than 150 sampling and analysis cycles during the week without any downtime.

6.1 XCEM Concentration

Figure 6-1 shows the individual measurements of each target metal made by the XCEM (diamonds) and the M29 measurement made at the same period (solid horizontal bars) taken from data shown in Appendix A. Lead concentrations are shown on two separate graphs, to more clearly show the lower concentrations seen in Runs 11 through 13. Also shown in Figure 6-1 are the XCEM readings on the palladium internal standard analyzed with every sample analysis. Average XCEM concentrations were calculated for each of the M29 runs according to Section 5.1. Table 6-1 summarizes the results of the XCEM measurements for each M29 run, showing the average XCEM and corresponding M29 results for each metal. The averages over all 13 runs are also shown in Table 6-1. Included also is the average for Runs 3 through 13. Runs 1 and 2 are excluded in this average because of the large lead concentrations that occurred from the M17 .50 caliber munitions that were used in those runs.

Table 6-1. Summary of Results from XCEM and M29 for Each Test Run

Run	Metal Concentration (µg/dscm)																	
	As		Ba		Cd		Cr		Hg		Ni		Pb		Sb		Zn	
	XCEM	M29	XCEM	M29	XCEM	M29	XCEM	M29	XCEM	M29	XCEM	M29	XCEM	M29	XCEM	M29	XCEM	M29
1	22	11	186	256	27	30	2	4	189	292	449	385	1169	1618	369	565	330	467
2	16	11	220	298	27	38	2	4	229	276	405	401	2498	3242	371	629	331	471
3	13	9	152	201	25	30	3	4	259	286	405	377	75	84	349	535	332	418
4	16	12	160	255	29	34	5	7	72	318	408	452	61	64	351	643	329	495
5	16	12	174	241	33	35	6	6	109	318	437	418	47	46	380	627	353	454
6	14	12	169	271	33	35	6	6	151	319	445	473	41	45	384	694	363	512
7	16	12	173	279	32	34	6	6	132	318	459	486	40	52	382	712	367	540
8	17	12	148	262	32	35	5	7	28	104	211	206	228	198	135	272	146	219
9	18	11	163	223	31	35	5	7	54	105	211	178	167	77	144	237	145	193
10	18	11	163	214	33	34	6	6	93	101	203	161	138	84	148	221	142	175
11	16	11	163	233	30	33	5	6	94	101	202	186	97	54	146	256	142	201
12	17	9	178	214	27	28	4	5	62	108	215	161	188	187	155	236	148	181
13	18	12	161	248	34	36	5	6	75	84	182	156	115	109	155	286	116	173
Average	17	11	170	246	30	34	5	6	119	210	325	311	374	451	267	455	250	346
Average (Runs 3-13)	16	11	164	240	31	33	5	6	103	197	307	296	109	91	248	429	235	324

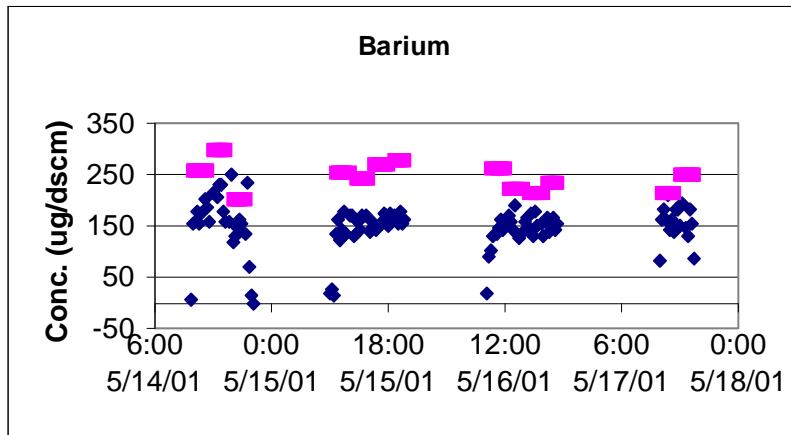
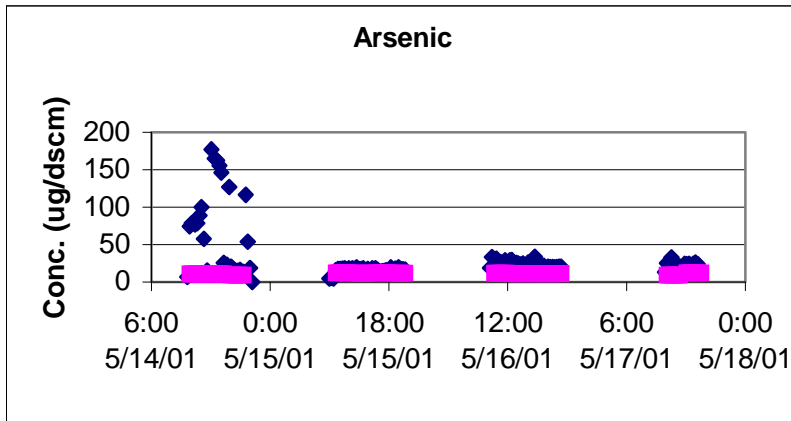
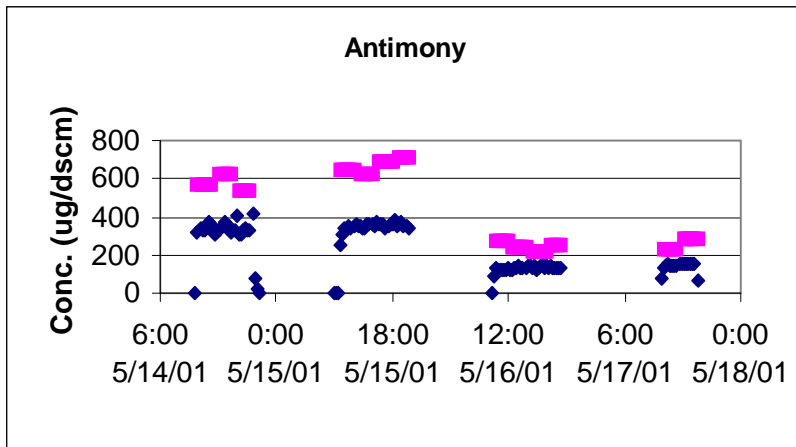


Figure 6-1. XCEM and M29 Data During Verification Test (diamonds = XCEM, bars = M29)

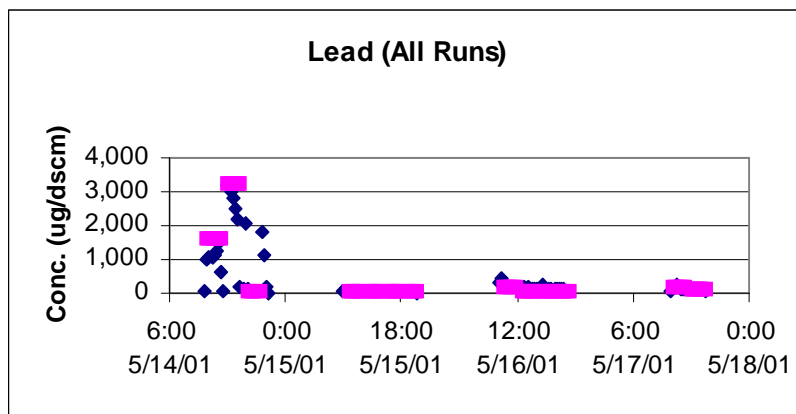
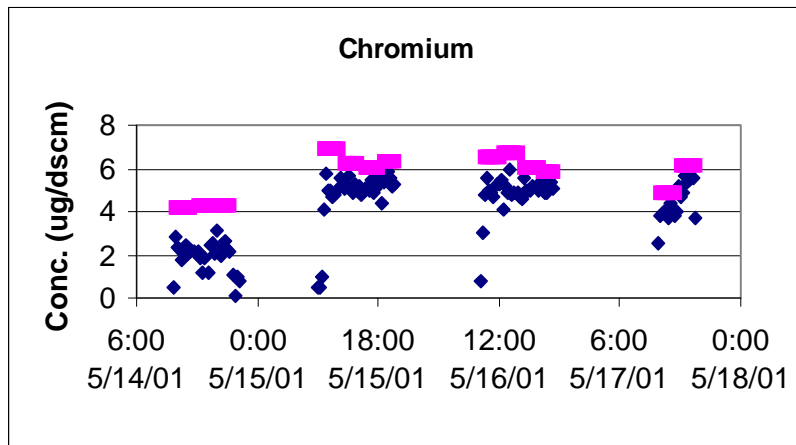
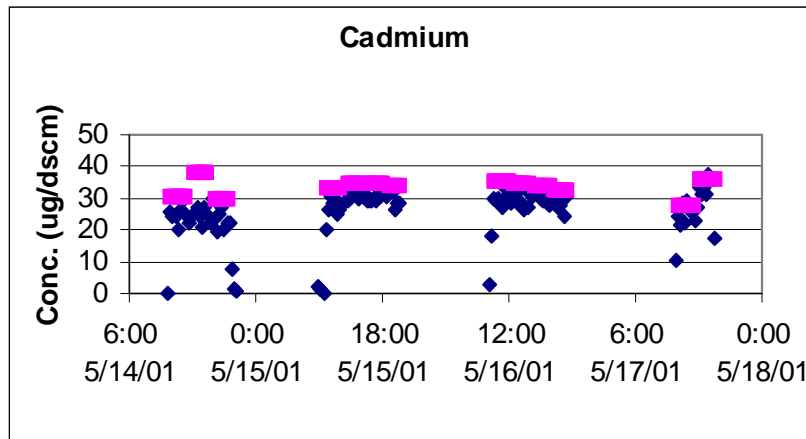


Figure 6-1. XCEM and M29 Data During Verification Test (diamonds = XCEM, bars = M29) (continued).

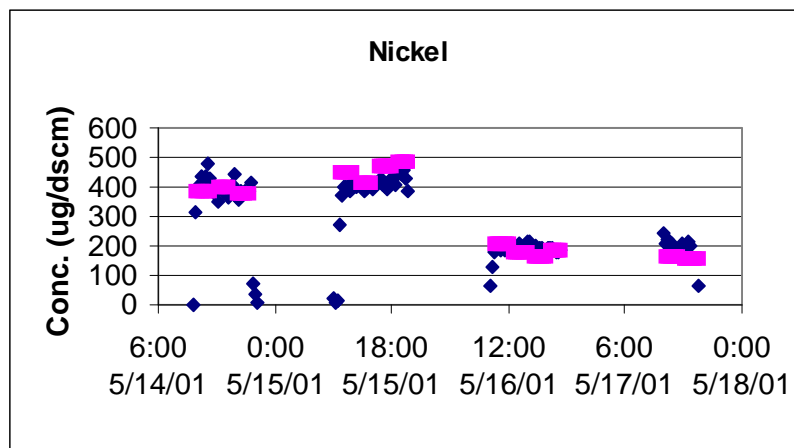
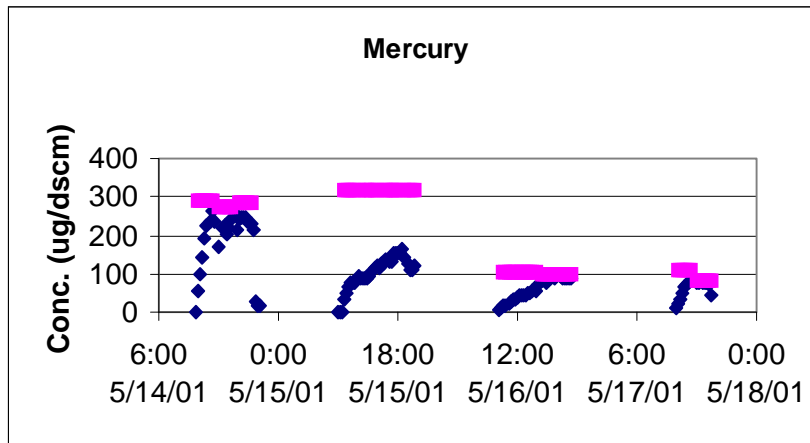
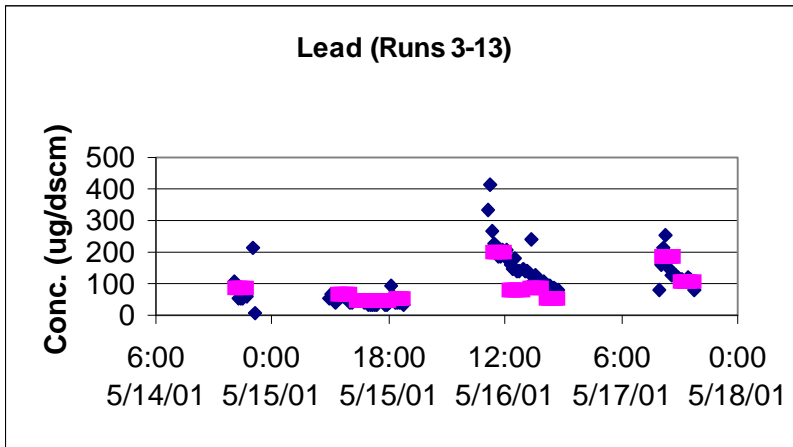


Figure 6-1. XCEM and M29 Data During Verification Test (diamonds = XCEM, bars = M29) (continued).

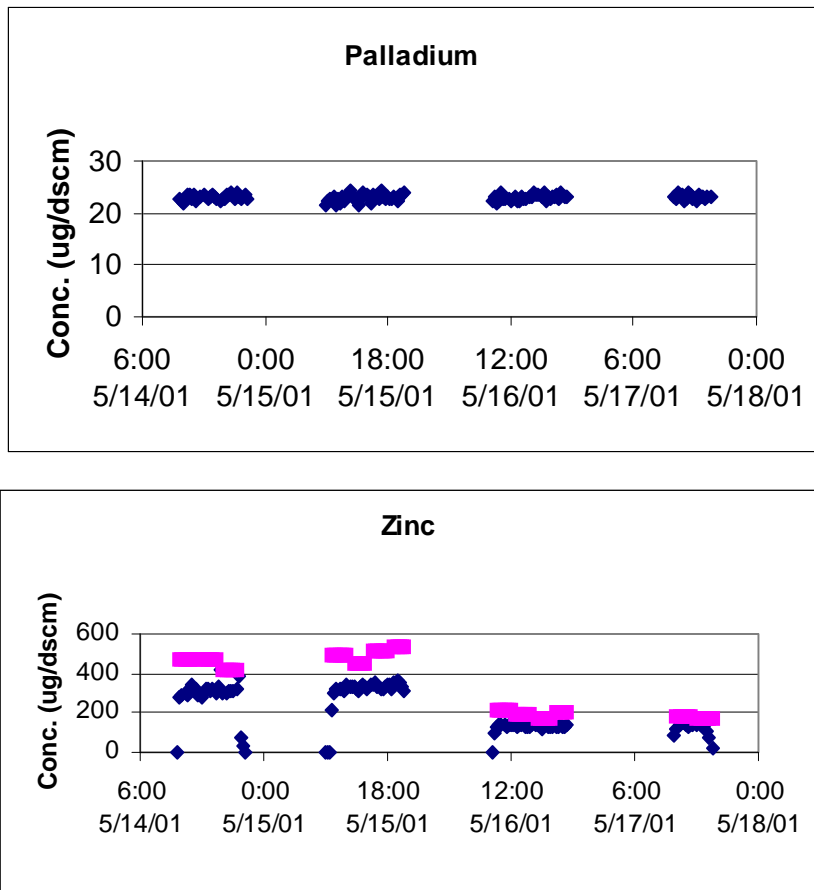


Figure 6-1. XCEM and M29 Data During Verification Test (diamonds = XCEM, bars = M29) (continued).

6.2 Relative Accuracy

Table 6-2 lists the percent RA results for all the target metals. These results are based on the XCEM and M29 results from all 13 test runs. In addition, RA for Pb and As also was calculated based on test Runs 3 through 13, thereby excluding the high Pb concentrations (and apparent interference in As measurement) in Runs 1 and 2. Because PS-10 allows basing the calculation of RA on nine runs, a recalculation of relative accuracy using Runs 3 through 7 and 10 through 13 also is presented. The following are specific comments on the RA results for each target metal.

As

An RA of 61.3% was found for As. Calculating RA using nine runs gave 53.1%. In general, the XCEM As concentrations were consistently higher than those measured by M29 (Figure 6-1). However, it was observed that XCEM As concentrations were highly correlated with XCEM Pb concentrations (Figure 6-2).

Table 6-2. Relative Accuracy Results for XCEM

Metal	RA (%)	RA (%) Using Nine Runs
As ^a	61.3	53.1
Ba	36.7	38.9
Cd	14.7	10.8
Cr	25.4	20.4
Hg	67.3	81.5
Ni	13.0	12.8
Pb ^b	54.8	36.7
Sb	53.5	58.6
Zn	36.8	39.4

^a Calculated RA of 52.8% using Runs 3-13 only.

^b Calculated RA of 46.1% using Runs 3-13 only.

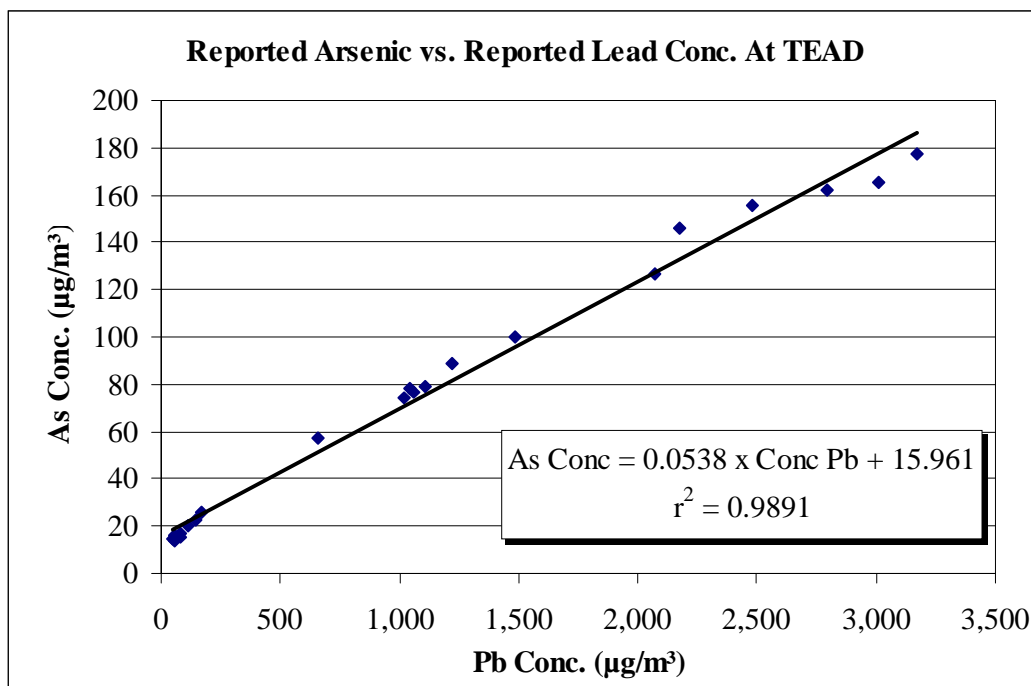


Figure 6-2. Uncorrected XCEM Arsenic Concentrations vs. XCEM Lead Concentrations

Since no significant As was expected in the background stack gas, and the As was spiked at a constant rate, the observed correlation is believed to be due to an XRF spectral interference. Concentrations of As are established by XRF using a K_{α} line, which is overlapped by the L_{α} line of Pb. For this reason, in XRF analysis, high Pb concentrations can interfere with As measurements, although the reverse is not true.

The XCEM vendor has indicated that a change in the spectral resolution approach can 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 previous tests of the XCEM, a calibration method was used that contained both As and Pb. No Pb/As interference was observed during those tests.⁽⁸⁾

Ba and Sb

Ba and Sb exhibited similar behavior during verification testing. For both metals, the average XCEM concentrations were significantly lower than the M29 reported concentrations, resulting in RAs of 36.7 and 53.5% for Ba and Sb, respectively.

Cd, Cr, and Ni

The agreement between XCEM and M29 reported concentrations for Cd, Cr, and Ni is illustrated in Figure 6-1 and reflects the RAs of 14.7% for Cd, 25.4% for Cr, and 13.0% for Ni.

Hg

As shown in Figure 6-1, at the beginning of each test day, the XCEM reported low Hg concentrations relative to M29. As the day progressed, the XCEM Hg reading usually gradually increased until it approximated M29 reported concentrations. This pattern suggests that the transport line from the stack to the XCEM was slowly equilibrating with the stack Hg level, and perhaps needed to be heated to a higher temperature to improve transmission efficiency. The M29 results showed that more than 98% 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. The majority (approximately 80%) of the sample was collected in the HNO_3 impinger, suggesting that most of the vapor-phase Hg was oxidized rather than elemental. This preponderance of oxidized Hg is consistent with the apparently slow equilibration of the XCEM inlet system each day. The overall RA for Hg was 67.3%; however, from Table 6-1, it can be seen that the XCEM Hg readings were within 20% of the M29 results on five runs (Runs 2, 3, 10, 11, and 13), all of which took place late in the day when equilibrium of the XCEM inlet line would be most nearly complete.

Pb

In general, the XCEM and M29 Pb concentrations were similar (Table 6-1 and Figure 6-1). Differences of about 25% were observed at the high Pb concentrations in Runs 1 and 2. Also, on May 16, both the XCEM and M29 Pb methods reported a higher Pb concentration at the start of the day than was observed on the previous day. The XCEM reported a consistent gradual decline

in Pb concentrations throughout the day on May 16, while M29 showed a more rapid decrease in concentration (Figure 6-1). On May 14, the XCEM was able to rapidly transition from high concentrations during Runs 1 and 2 to a much lower concentration during Run 3 and agreed with M29 for that third run (Table 6-1). The May 14 XCEM/M29 comparisons indicate that the XCEM is responsive to rapid changes in Pb concentration and is resistant to sample line contamination.

Overall, the XCEM achieved an RA for Pb of 54.8% for all 13 runs and an RA of 46.1% when only Runs 3 to 13 were considered. Runs 1, 2, 9, 10, and 11 had the greatest influence on the RA values. Calculating RA using only nine runs gave an RA of 36.7%.

Zn

Like Ba and Sb, the XCEM Zn concentrations were consistently lower than the M29 concentrations (Figure 6-1). An RA of 36.8% was found for Zn.

6.3 Correlation with Reference Method

The degree of correlation between the XCEM and M29 is shown in Figure 6-3 and summarized in Table 6-3. Five metals were present in the stack gas at sufficiently varying concentrations to support a calculation of correlation, i.e., Hg, Ni, Pb, Sb, and Zn. Of these elements, Ni, Pb, Sb, and Zn show coefficients of determination (r^2) of 0.95 or better. The correlation for Pb was weaker over Runs 3 through 13 ($r^2 = 0.75$) than when all 13 runs were included ($r^2 = 0.997$) as a result of the influence of the high Pb levels in Runs 1 and 2. Hg did not show a high correlation between the two methods ($r^2=0.388$) possibly due to the postulated inlet losses during sampling.

6.4 Precision

The XCEM precision results are presented in Table 6-4 for each target metal, and for the Pd internal standard, for each M29 run. Precision was calculated in terms of the percent RSD of a series of XCEM measurements made during stable operation of the TEAD incinerator, with metals injected at a constant rate. Therefore, precision reflects not only the XCEM variability, but also the variability in the stack concentrations, spiking rate, and flow variability.

Table 6-4 shows that average results for Ba, Cd, Cr, Ni, Sb, and Zn were in the range of 6 to 12% RSD; and, for these metals, very few RSD values exceeded 15%. Run 13 produced the highest RSD values for several of these metals. As (16% RSD), Hg (18% RSD), and Pb (21% RSD) exhibited higher average RSD values. The average percent RSD for As was strongly affected by the result from Run 2 (65% RSD); excluding that value, an average of 11.9% RSD would result. For Hg, the percent RSD values from the first run on each test day (i.e., Runs 1, 4, 8, and 12) ranged from 30 to 44%, whereas all other percent RSD values ranged from 3 to 18%, and averaged 9.6%. Thus, the precision for Hg was strongly influenced by the sampling difficulties noted above that occurred at the start of each test day. For Pb, percent RSD values were generally

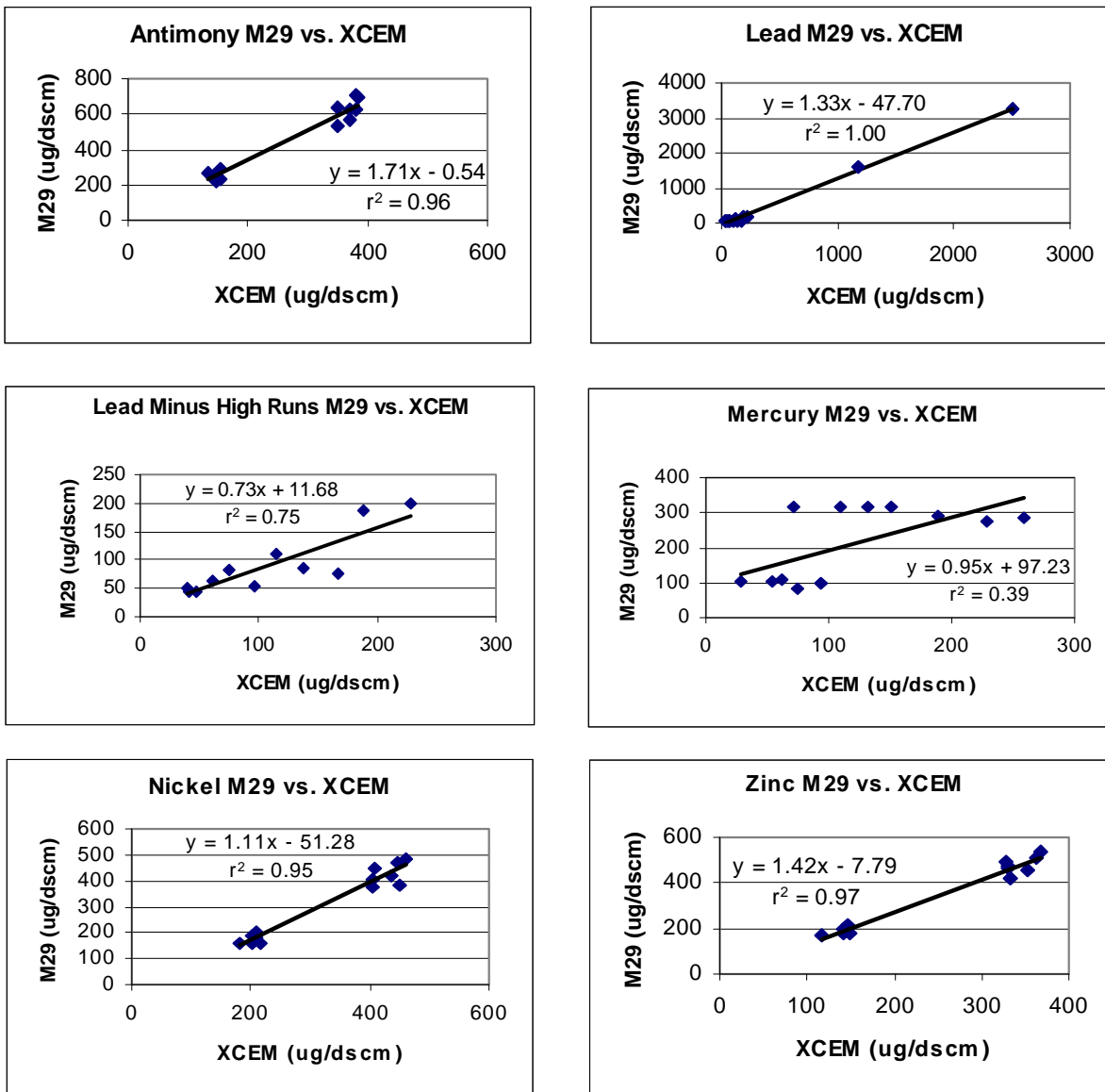


Figure 6-3. Correlation Between XCEM and M29

Table 6-3. Correlation Between XCEM and M29

Element	r	Correlation (r^2)
Hg	0.623	0.388
Ni	0.976	0.953
Pb	0.998	0.997
Sb	0.980	0.960
Zn	0.987	0.973

Table 6-4. XCEM Precision

Run	Percent RSD									
	As	Ba	Cd	Cr	Hg	Ni	Pb	Sb	Zn	Pd
1	8	11	11	16	44	12	23	5	8	3
2	65	14	10	30	11	5	48	5	6	2
3	10	12	12	16	3	3	33	4	3	2
4	9	14	14	10	30	13	14	11	13	3
5	8	7	5	5	13	3	12	3	3	3
6	13	7	6	6	9	3	13	2	3	3
7	7	7	8	6	10	6	16	4	6	3
8	14	14	6	6	34	6	14	4	4	3
9	12	15	7	11	9	5	10	4	2	2
10	16	13	8	4	9	5	41	6	5	2
11	5	8	8	8	6	4	8	2	2	2
12	16	15	11	6	40	7	27	6	6	3
13	25	24	21	14	18	30	12	22	42	2
Average	16	12	10	11	18	8	21	6	8	2

higher and more variable than for other elements. Values as high as 41% RSD were found, even excluding the first two test runs. As noted above, this may be due in part to real variability in the lead level in the stack gas.

6.5 Span, Zero, and Internal Standard Drift

Span and zero checks were conducted on each of the four test days, with the results shown in Table 6-5. Since the span and zero checks are evaluations of mass measurement results, they are reported as mass per unit area on the filter ($\mu\text{g}/\text{spot}$). Equivalent span and zero concentrations in micrograms per dry standard cubic meter also are shown in Table 6-5 and reflect the typical sampling rate of 16 liters per spot.

Table 6-5. XCEM Span and Zero Readings During Verification Testing

Date	Span Readings (µg)				Zero Readings (µg) ¹			
	Cd	Cr	Hg	Pb	Cd	Cr	Hg	Pb
5/14/01	156	5.23	27.6	30.4	0.024	0.012	0.008	0.008
5/15/01	158	5.53	28.0	30.9	0.024	0.016	0.008	0.008
5/16/01	156	5.45	27.9	30.8	0.024	0.014	0.008	0.008
5/17/01	156	5.42	27.9	30.6	0.024	0.006	0.008	0.023
Average	157	5.41	27.8	30.7	0.024	0.012	0.008	0.018
Date	Equiv. Span Values (µg/dscm) ²				Equiv. Zero Values (µg/dscm) ^{1,2}			
	Cd	Cr	Hg	Pb	Cd	Cr	Hg	Pb
5/14/01	9,765	327	1,724	1,898	1.50	0.75	0.50	0.50
5/15/01	9,850	346	1,750	1,931	1.50	1.01	0.50	0.50
5/16/01	9,772	341	1,742	1,925	1.50	0.85	0.50	0.50
5/17/01	9,744	339	1,746	1,912	1.50	0.38	0.50	1.44
Average	9,783	338	1,741	1,917	1.50	0.75	0.50	0.73
SD	46.14	7.88	11.25	14.64				
% RSD	0.47	2.33	0.65	0.76				

¹ Shaded values were nondetects. Nondetect treated as ½ of detection limit.

² Equivalent concentrations determined assuming 16 liters of gas sampled. The span check indicated no trend in span results and good precision over the four days of testing. The precision (as percent RSD) of the span results over the four days was less than 1% for Cd, Hg, and Pb and about 2.3% for Cr.

The XCEM span readings show no significant trend with time and exhibit percent RSD values of 0.47 to 2.33. These results show that day-to-day variation in the XCEM span response was minimal over the four test days.

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

The Pd internal standard, which is measured with every sample, also displayed stable readings and good precision over the four days of testing (Figure 6-4). Overall, the Pd reading had a precision (percent RSD) of approximately 2.5%, with all 113 measured Pd readings lying within 6% of the average reading. Analysis of the Pd trend in Figure 6-4 indicates that no significant drift occurred, i.e., over the four-day test period, the average daily Pd reading changed by less than 1.0%.

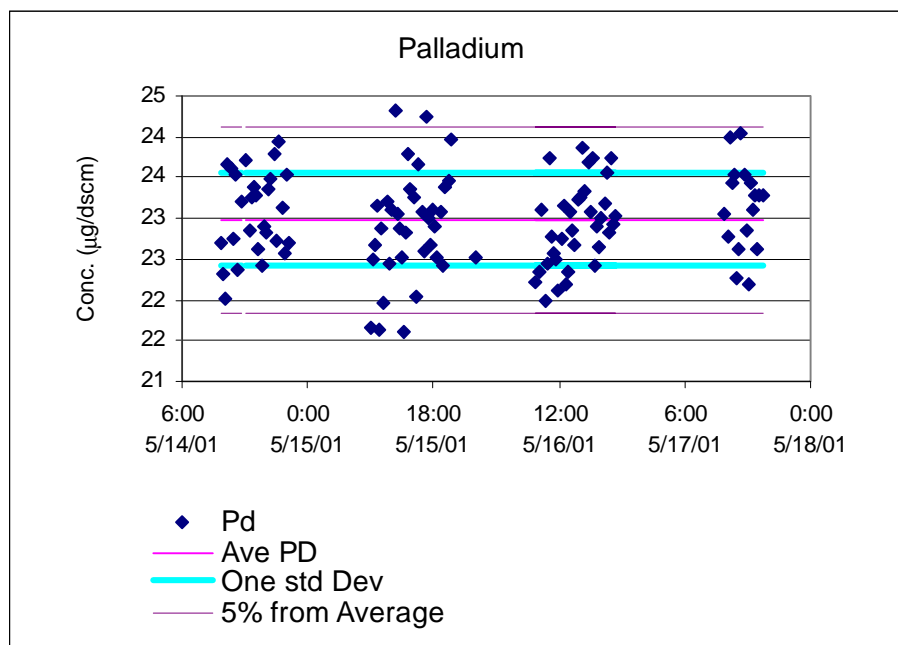


Figure 6-4. XCEM Palladium Internal Standard Readings During M29 Testing

6.6 XCEM Bias Relative to M29

Using the M301 approach, the XCEM results for all the target metals were found to be significantly biased relative to the corresponding results from M29, as shown in Table 6-6. Thus, a significant positive and negative bias was found even for Cd, Cr, and Ni, for which the overall average concentrations determined by the XCEM differed little from those determined by M29 (see Table 6-1).

6.7 Response Time

The XCEM sampled continuously except for a four-second period between each 20-minute sample run when the filter tape was moved to a new analysis position. Thus, the cycle time for the XCEM as a batch analyzer is 20 minutes and 4 seconds. Also, XCEM results are reported immediately after analysis, resulting in a 20-minute lag time between the end of sampling and reporting.

Table 6-6. XCEM Bias Relative to M29

Element	t-stat	t-critical	Significant Bias
As	8.8068	1.356	Yes
Ba	11.4506	1.356	Yes
Cd	4.15447	1.356	Yes
Cr	6.28591	1.356	Yes
Hg	3.92706	1.356	Yes
Ni	6.16179	1.356	Yes
Pb	1.77641	1.356	Yes
Sb	7.42625	1.356	Yes
Zn	6.81789	1.356	Yes

Chapter 7 Performance Summary

In comparisons with results from M29, the XCEM relative accuracy for Cd, Cr, and Ni was less than 26%. The remaining metals (As, Ba, Hg, Pb, Sb, and Zn) had RA values between 37 and 67%. The reported XCEM concentrations were uniformly high for As. The XCEM was consistently low for Zn, Ba, and Sb. XCEM Hg readings were very low at the start of each test day, rising gradually until they stabilized. This behavior is possibly a result of equilibration of the XCEM inlet line with vapor phase mercury. The best agreement of XCEM and M29 Hg results (within about 20%) was found with M29 runs conducted late in the test day, when XCEM readings had stabilized. When calculated using nine runs, the RA for Cd, Cr, and Ni was between 11 and 20% and the remaining metals had an RA between 36% (Pb) and 82% (Hg).

Correlation of XCEM and M29 results was calculated for five elements that varied enough during the test to justify this comparison. For Ni, Pb, Sb, and Zn, r^2 values exceeding 0.95 were found, although the r^2 value for Pb decreased to 0.75 when the high Pb levels in Runs 1 and 2 were excluded. For Hg, an r^2 value of 0.39 was found, due, in part, to the equilibration issue noted above.

The XCEM's precision, as RSD of successive readings with stable metal concentrations, ranged from 6 to 21% over the nine target metals. This precision includes variability in the metals injection and the test facility, as well as in the XCEM itself.

XCEM span and zero drift were assessed over the four test days. Daily span readings of Cd, Cr, Hg, and Pb exhibited percent RSD values of 0.47 to 2.33 and no significant trends over time. Zero readings for all four elements were near or below the respective detection limits on all test days. The RSD of the XCEM's Pd internal standard was approximately 2.5%, with no significant trend over time.

The XCEM results showed statistically significant positive and negative bias relative to M29 results for all the target metals, based on M301 procedures.

The XCEM functioned in an automated manner and automatically recorded concentrations, temperatures, flow rates, and QA data. It exhibited no mechanical problems, had an effective up-time of 100%, and a response time of 20 minutes.

Chapter 8 References

1. Progressive Software, Albany, Oregon, 2001.
2. *Test/QA Plan for Pilot-Scale Verification of Continuous Emission Monitors for Multi-Metals*, Battelle, Columbus, Ohio, May 2001.
3. *Determination of Metal Emissions from Stationary Sources*, U.S. Environmental Protection Agency, Method 29, February 2000.
4. *Field Validation of Pollutant Measurement Methods from Various Waste Media*, U.S. Environmental Protection Agency, Method 301, December 1992.
5. *Stack Spiking Report for a Multi-Metals CEMS Test at the Tooele Army Depot Deactivation Furnace*, prepared for U.S. Army Corps of Engineers by MSE Technology Applications, Inc., Butte, Montana, June 2001.
6. *Verification of Multi-Metals Continuous Emission Monitor at Tooele Army Depot*. Air Pollution Management Study No. 43-EL-6498-01, Tooele, Utah, May 14-17, 2001, prepared by the U.S. Army Center for Health Promotion and Preventive Medicine, 2001.
7. *Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Pilot*, Version 2.0, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, October 2000.
8. Johnsen, B., J. Cooper, A. C. Milliken. *X-Ray Fluorescence Multi-Metals Monitor Data Recording and Calibration Automation and Mercury Sampling*, prepared for U.S. Army Corps of Engineers by CES, Beaverton, Oregon, Contract No. DACA42-00-P-0245, 2000.

Appendix A

XCEM Data During M29 Runs

Appendix A

XCEM Data During M29 Runs

Date	Start	Stop	XC No.	RM No.	As	Ba	Cd	Cr	Hg	Ni	Pb	Sb	Zn	Pd
					(micrograms/dscm)									
05/14/2001	10:45	11:05	650	Run 1	20.8	166	27.7	3.1	59	343	1,102	340	297	24.1
05/14/2001	11:05	11:26	651	Run 1	24.3	171	26.0	2.5	109	436	1,127	372	316	23.8
05/14/2001	11:26	11:48	652	Run 1	21.1	192	26.5	1.9	156	467	1,149	361	320	25.6
05/14/2001	11:48	12:09	653	Run 1	20.7	165	21.8	2.2	207	449	1,196	353	316	25.5
05/14/2001	12:10	12:31	654	Run 1	25.3	187	28.2	2.6	242	470	1,319	377	342	24.6
05/14/2001	12:31	12:53	655	Run 1	21.5	218	31.8	2.2	257	515	1,607	399	372	25.4
05/14/2001	12:53	13:15	656	Run 1	23.8	202	27.2	2.4	283	463	709	386	348	24.2
05/14/2001	13:58	14:23	659	Run 2	7.3	230	26.8	2.3	186	375	3,422	360	299	25.6
05/14/2001	14:23	14:46	660	Run 2	3.5	224	29.5	2.0	234	427	3,248	379	345	24.7
05/14/2001	14:46	15:09	661	Run 2	13.0	249	26.0	1.2	244	427	3,017	398	352	25.1
05/14/2001	15:09	15:32	662	Run 2	23.8	250	22.3	2.0	220	405	2,683	370	332	25.3
05/14/2001	15:32	15:55	663	Run 2	31.5	194	29.1	1.2	239	415	2,347	379	347	25.2
05/14/2001	15:55	16:17	664	Run 2	17.8	172	27.1	2.6	257	392	182	348	319	24.4
05/14/2001	17:00	17:23	667	Run 3	15.3	127	25.4	3.4	259	395	118	334	320	24.6
05/14/2001	17:23	17:44	668	Run 3	13.1	140	21.3	2.2	264	388	91	335	319	25.2
05/14/2001	17:44	18:05	669	Run 3	13.0	158	27.0	2.5	265	417	60	355	341	25.4
05/14/2001	18:05	18:26	670	Run 3	13.1	175	28.9	2.9	268	409	55	363	339	25.7
05/14/2001	18:26	18:47	671	Run 3	14.2	168	21.4	2.4	255	413	60	352	333	24.6
05/14/2001	18:47	19:07	672	Run 3	11.2	147	24.0	2.3	249	414	65	360	347	25.9
05/15/2001	8:59	9:18	684	Run 4	13.2	145	21.5	4.5	33	294	69	271	235	25.0

Date	Start	Stop	XC No.	RM No.	As	Ba	Cd	Cr	Hg	Ni	Pb	Sb	Zn	Pd
					(micrograms/dscm)									
05/15/2001	9:18	9:39	685	Run 4	15.0	173	28.5	6.2	54	401	69	333	319	23.4
05/15/2001	9:39	10:00	686	Run 4	15.6	133	33.2	5.4	69	432	66	362	349	24.7
05/15/2001	10:00	10:21	687	Run 4	16.2	154	30.5	5.3	80	432	64	371	348	23.7
05/15/2001	10:21	10:42	688	Run 4	16.6	191	32.1	5.0	84	433	64	378	344	25.1
05/15/2001	10:42	11:03	689	Run 4	15.2	145	26.6	5.2	85	418	55	361	339	24.2
05/15/2001	11:03	11:24	690	Run 4	17.4	183	28.5	5.5	98	446	45	380	366	25.0
05/15/2001	12:06	12:27	693	Run 5	18.0	177	31.4	5.5	93	440	49	383	355	24.7
05/15/2001	12:27	12:48	694	Run 5	16.2	172	33.7	5.5	97	430	54	371	348	24.3
05/15/2001	12:48	13:09	695	Run 5	16.0	153	34.4	6.1	102	417	52	362	339	23.3
05/15/2001	13:09	13:30	696	Run 5	17.3	182	33.4	5.3	114	450	47	386	360	24.6
05/15/2001	13:30	13:51	697	Run 5	14.3	185	35.8	5.7	122	449	45	393	365	25.7
05/15/2001	13:51	14:12	698	Run 5	17.0	181	32.2	5.4	129	443	38	390	358	25.2
05/15/2001	14:54	15:15	701	Run 6	17.8	166	31.4	5.4	137	455	39	392	376	25.6
05/15/2001	15:15	15:36	702	Run 6	15.5	152	31.9	5.4	146	465	39	386	379	24.9
05/15/2001	15:36	15:57	703	Run 6	12.4	167	31.4	5.4	142	443	48	387	362	24.4
05/15/2001	15:57	16:18	704	Run 6	12.9	165	31.3	5.9	140	430	47	372	350	26.2
05/15/2001	16:18	16:39	705	Run 6	14.0	187	34.1	5.3	168	427	36	381	353	24.9
05/15/2001	16:39	17:00	706	Run 6	15.2	185	32.9	5.5	164	442	35	389	363	24.5
05/15/2001	17:00	17:21	707	Run 6	13.7	164	36.7	6.2	166	462	46	387	369	25.0
05/15/2001	18:03	18:24	710	Run 7	16.9	183	35.6	5.8	154	477	45	396	386	24.9
05/15/2001	18:24	18:45	711	Run 7	18.5	166	34.5	6.4	134	478	44	404	395	24.2
05/15/2001	18:45	19:06	712	Run 7	16.5	191	28.8	6.0	120	491	45	377	377	25.3
05/15/2001	19:06	19:27	713	Run 7	16.1	168	30.9	5.6	121	459	40	375	359	25.3
05/15/2001	19:27	19:48	714	Run 7	16.2	175	30.7	5.7	132	419	34	367	337	25.9
05/15/2001	19:48	20:09	715	Run 7	15.1	159	33.3	5.5	137	436	30	379	351	24.3
05/16/2001	8:58	9:18	725	Run 8	17.6	111	32.5	5.2	17	193	290	141	134	23.8
05/16/2001	9:18	9:39	726	Run 8	20.3	139	31.8	6.0	20	220	242	134	150	24.2
05/16/2001	9:39	10:00	727	Run 8	16.5	145	32.3	5.4	22	222	231	125	151	25.6
05/16/2001	10:00	10:20	728	Run 8	18.0	156	29.4	5.3	28	197	199	136	148	24.6

Date	Start	Stop	XC No.	RM No.	As	Ba	Cd	Cr	Hg	Ni	Pb	Sb	Zn	Pd
					(micrograms/dscm)									
05/16/2001	10:20	10:41	729	Run 8	12.5	176	36.3	5.1	33	204	202	135	141	24.4
05/16/2001	10:41	11:01	730	Run 8	18.7	152	32.7	5.7	36	216	226	134	150	24.3
05/16/2001	11:01	11:22	731	Run 8	17.1	162	32.4	5.7	44	226	214	141	150	23.9
05/16/2001	11:42	12:03	733	Run 9	21.1	183	33.1	4.5	49	210	190	136	147	25.0
05/16/2001	12:03	12:23	734	Run 9	14.8	170	32.7	5.6	50	201	170	139	142	24.0
05/16/2001	12:23	12:44	735	Run 9	18.8	154	30.7	5.3	49	204	162	142	146	24.1
05/16/2001	12:44	13:04	736	Run 9	16.6	206	35.4	6.5	56	223	191	154	152	24.9
05/16/2001	13:04	13:25	737	Run 9	17.0	143	31.1	5.2	54	215	151	145	145	24.7
05/16/2001	13:25	13:45	738	Run 9	18.6	138	28.8	5.2	59	200	153	145	144	24.5
05/16/2001	13:45	14:05	739	Run 9	16.0	151	29.1	5.2	60	228	155	148	143	25.1
05/16/2001	14:46	15:07	742	Run 10	19.2	156	34.7	6.0	91	210	146	148	146	25.2
05/16/2001	15:07	15:27	743	Run 10	22.3	187	37.0	5.4	89	216	261	154	151	25.6
05/16/2001	15:27	15:48	744	Run 10	17.0	141	32.5	5.4	82	192	115	134	133	24.9
05/16/2001	15:48	16:08	745	Run 10	17.1	192	31.6	5.4	91	208	134	146	149	25.6
05/16/2001	16:08	16:28	746	Run 10	17.5	161	36.2	5.5	95	208	108	163	145	24.2
05/16/2001	16:29	16:49	747	Run 10	18.3	167	30.9	5.6	95	203	95	140	137	24.7
05/16/2001	16:49	17:09	748	Run 10	12.7	139	29.9	5.4	109	186	110	152	137	24.5
05/16/2001	17:32	17:52	750	Run 11	15.7	178	31.3	6.0	101	211	108	150	143	25.0
05/16/2001	17:52	18:12	751	Run 11	15.8	147	30.2	5.2	96	209	102	147	141	25.5
05/16/2001	18:12	18:33	752	Run 11	15.5	170	29.3	5.3	95	204	104	141	145	24.6
05/16/2001	18:33	18:53	753	Run 11	16.4	178	30.2	5.4	95	192	91	147	138	25.6
05/16/2001	18:53	19:13	754	Run 11	17.3	152	26.4	5.8	96	191	89	147	141	24.8
05/16/2001	19:13	19:34	755	Run 11	17.2	167	32.8	5.5	92	201	89	143	146	24.9
05/16/2001	19:34	19:54	756	Run 11	15.0	152	33.2	4.6	84	212	96	147	145	24.0
05/17/2001	11:12	11:32	770	Run 12	17.8	174	26.5	4.1	24	224	170	137	133	24.6
05/17/2001	11:32	11:52	771	Run 12	17.2	195	23.2	4.2	35	238	232	159	146	25.9
05/17/2001	11:52	12:12	772	Run 12	20.5	174	30.5	4.3	55	222	273	165	157	25.3
05/17/2001	12:12	12:32	773	Run 12	16.7	226	24.4	4.0	73	221	204	158	161	25.4
05/17/2001	12:32	12:53	774	Run 12	18.4	153	31.7	4.8	79	206	161	158	151	24.1

Date	Start	Stop	XC No.	RM No.	As	Ba	Cd	Cr	Hg	Ni	Pb	Sb	Zn	Pd
					(micrograms/dscm)									
05/17/2001	12:53	13:13	775	Run 12	12.3	177	28.0	4.5	83	204	138	155	143	24.4
05/17/2001	13:13	13:33	776	Run 12	14.1	150	28.2	4.1	86	191	140	155	151	26.0
05/17/2001	14:14	14:34	779	Run 13	19.1	162	35.9	5.1	80	201	119	171	146	24.0
05/17/2001	14:34	14:54	780	Run 13	19.9	210	33.9	5.3	80	213	122	170	146	25.3
05/17/2001	14:54	15:14	781	Run 13	17.4	159	36.1	6.1	82	235	117	168	149	25.0
05/17/2001	15:14	15:34	782	Run 13	20.3	140	33.8	5.8	83	212	112	170	150	25.1
05/17/2001	15:35	15:55	783	Run 13	21.3	196	40.7	5.9	84	173	129	169	117	24.4
05/17/2001	15:55	16:15	784	Run 13	19.2	165	39.1	6.0	74	170	121	166	82	25.1
05/17/2001	16:15	16:35	785	Run 13	8.3	94	18.7	4.0	46	70	85	77	22	25.2