SUBTASK 4.27 – EVALUATION OF THE MULTIELEMENT SORBENT TRAP (MEST) METHOD AT AN ILLINOIS COAL-FIRED PLANT

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National Energy Technology Laboratory
U.S. Department of Energy
626 Cochrans Mill Road
PO Box 10940, MS 921-107
Pittsburgh, PA 15236-0940

Cooperative Agreement No.: DE-FC26-08NT43291
DOE Technical Monitor: Barbara Carney

Prepared by:

John H. Pavlish
Jeffrey S. Thompson
Grant E. Dunham

Energy & Environmental Research Center
University of North Dakota
15 North 23rd Street, Stop 9018
Grand Forks, ND 58202-9018

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SUBTASK 4.27 – EVALUATION OF THE MULTIELEMENT SORBENT TRAP (MEST) METHOD AT AN ILLINOIS COAL-FIRED PLANT

ABSTRACT

Owners of fossil fuel-fired power plants face the challenge of measuring stack emissions of trace metals and acid gases at much lower levels than in the past as a result of increasingly stringent regulations. In the United States, the current reference methods for trace metals and halogens are wet-chemistry methods, U.S. Environmental Protection Agency (EPA) Methods 29 and 26 or 26A, respectively. As a possible alternative to the EPA methods, the Energy & Environmental Research Center (EERC) has developed a novel multielement sorbent trap (MEST) method to be used to sample for trace elements and/or halogens. Sorbent traps offer a potentially advantageous alternative to the existing sampling methods, as they are simpler to use and do not require expensive, breakable glassware or handling and shipping of hazardous reagents. Field tests comparing two sorbent trap applications (MEST-H for hydrochloric acid and MEST-M for trace metals) with the reference methods were conducted at two power plant units fueled by Illinois Basin bituminous coal. For hydrochloric acid, MEST measured concentrations comparable to EPA Method 26A at two power plant units, one with and one without a wet flue gas desulfurization scrubber. MEST-H provided lower detection limits for hydrochloric acid than the reference method. Results from a dry stack unit had better comparability between methods than results from a wet stack unit. This result was attributed to the very low emissions in the latter unit, as well as the difficulty of sampling in a saturated flue gas. Based on these results, the MEST-H sorbent traps appear to be a good candidate to serve as an alternative to Method 26A (or 26). For metals, the MEST trap gave lower detection limits compared to EPA Method 29 and produced comparable data for antimony, arsenic, beryllium, cobalt, manganese, selenium, and mercury for most test runs. However, the sorbent material produced elevated blanks for cadmium, nickel, lead, and chromium at levels that would interfere with accurate measurement at U.S. hazardous air pollutant emission limits for existing coal-fired power plant units. Longer sampling times employed during this test program did appear to improve comparative results for these metals. Although the sorbent contribution to the sample was reduced through improved trap design, additional research is still needed to explore lower-background materials before the MEST-M application can be considered as a potential alternative method for all of the trace metals.

This subtask was funded through the EERC–U.S. Department of Energy Joint Program on Research and Development for Fossil Energy-Related Resources Cooperative Agreement No. DE-FC26-08NT43291. Nonfederal funding was provided by the Electric Power Research Institute, the Illinois Clean Coal Institute, Southern Illinois Power Company, and the Center for Air Toxic Metals Affiliates Program.

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SI CONVERSION FACTORS

	English (US) units	×	Factor	=	SI units
Area:	1 ft^2	×	9.29×10^{-2}	=	m^2
Flow Rate:	1 gal/min	×	6.31×10^{-5}	=	m^3/s
	1 gal/min	×	6.31×10^{-2}	=	L/s
Length:	1 ft	×	0.3048	=	m
	1 in	×	2.54	=	cm
	1 yd	×	0.9144	=	m
Mass:	1 lb	×	454	=	g
	1 lb	×	0.454	=	kg
	1 gr	×	0.0648	=	g
	1 ton	×	0.907		tonne
Volume:	1 ft^3	×	28.3	=	L
	1 ft^3	×	0.0283	=	m^3
	1 gal	×	3.785	=	L
	1 gal	×	3.785×10^{-3}	=	m^3
Temperature:	°F −32	×	0.556	=	°C
Energy:	Btu	×	1055.1	=	joule
	TBtu	×	1055.1×10^{-9}	=	kJ
	Btu/hr	×	0.29307	=	watt
Mass/Energy:	lb/Btu	×	2.325	=	kg/kJ

NONMENCLATURE

ARL	Analytical Research Laboratory
ASTM	American Society for Testing Materials
CCV	continuing calibration verification
CEM	continuous emission monitor
CVAAS	cold-vapor atomic absorption spectroscopy
DOE	U.S. Department of Energy
EERC	Energy & Environmental Research Center
EGU	electric generating unit
EPA	U.S. Environmental Protection Agency
EPRI	Electric Power Research Institute
Eq	equivalent
ESP	electrostatic precipitator
FGD	flue gas desulfurization
GFAAS	graphite furnace atomic absorption spectroscopy
GWh	gigawatt hour
HAP	hazardous air pollutant
HBr	hydrogen bromide
IC	ion chromatography
ICP–MS	inductively coupled plasma–mass spectroscopy
ICV	initial calibration verification
LOQ	limit of quantitation
M29	EPA Method 29
MATS	Mercury and Air Toxics Standard
MDL	method detection limit
MEST	multielement sorbent trap
MEST-H	multielement sorbent trap (halogens)
MEST-M	multielement sorbent trap (multimetals)
mg/L	milligram per liter
mm	millimeter
MMBtu	million British thermal unit
MWh	megawatt hour
NIST	National Institute of Standards and Technology
ppmv	parts per million by volume
ppmvd	parts per million by volume, dry basis
QA/QC	quality assurance/quality control
RD	relative difference
RSD	relative standard deviation
TBtu	trillion British thermal unit
$\mu g/dNm^3$	micrograms per dry normal cubic meter

SUBTASK 4.27 – EVALUATION OF THE MULTIELEMENT SORBENT TRAP (MEST) METHOD AT AN ILLINOIS COAL-FIRED PLANT

EXECUTIVE SUMMARY

Over the past two decades, emissions of mercury, nonmercury metals, and acid gases from energy generation have become the focus of regulatory rule making. On February 16, 2012, the U.S. Environmental Protection Agency (EPA) promulgated the Mercury and Air Toxics Standards (MATS) to reduce mercury, nonmercury metals, and HCl emissions from coal-fired power plants {National Emission Standards for Hazardous Air Pollutants from Coal- and Oil-Fired Electric Utility Steam Generating Units and Standards of Performance for Fossil-Fuel-Fired Electric Utility, Industrial-Commercial-Institutional, and Small Industrial-Commercial-Institutional Steam Generating Units: Final Rule (Mercury and Air Toxics Standards [MATS]). 40 Code of Federal Regulations, Parts 60 and 63; *Fed. Regist*. **2012**, *77* (32), 9304}. The standard sets limits on mercury, nonmercury metal, and acid gas (HCl, and for oil units, hydrofluoric acid) emissions from new and existing coal- and oil-fired power plant units. After the compliance deadline (2015, or later if a waiver is given), coal- and oil-fired electric generating units (EGUs) will have to measure and report emissions and maintain emissions below specified limits. The reference measurement method for halogens is EPA Method (M) 26 (nonisokinetic) or M26A (isokinetic). They are wet-chemistry, impinger-based methods that are designed to collect both acid gas and halogen gas species present in flue gas. The reference method for mercury and nonmercury metal HAPs is EPA M29, also an impinger-based method. There are a number of concerns regarding the use of EPA M26/26A and EPA M29 to meet the MATS requirements, including the following:

1. The EPA methods are difficult to use, require highly trained personnel, and involve substantial preparation.
2. The methods utilize toxic chemicals that are a concern for safety, shipping, and ultimate disposal.
3. A very high level of quality control is required, not only for sample analysis but for the sample-collecting activities.
4. The detection limits for EPA Method 29 may not be adequate in some cases to measure accurately at the existing unit limits established under MATS.
5. Inclusion of mercury in a Method 29 test creates a risk of contaminating the sample with Mn, because of the additional permanganate impinger that must be added to the sampling train.

As a potential alternative to EPA Method 29 and EPA Method 26/26A, the Energy & Environmental Research Center (EERC) developed a multielement sorbent trap (MEST) method with two separate sampling applications: one for metals (MEST-M) and one for halogens (MEST-H). The overall goal of this project was to evaluate the applicability and performance of the MEST method for measuring trace metal and HCl emissions at two power plant units that burn Illinois Basin coal.

A comparative study of the MEST-H method and EPA M26/M26A was performed for the two power plants. Sampling at the two units presented relatively high and low HCl emission

levels, challenging the MEST-H over a wide range. A statistical analysis was used to compare the relative bias and precision of the two methods. Results of the comparison indicated no significant bias for HCl by MEST-H compared to Method 26A, based on EPA Method 301 criteria. At both units, the HCl emission measurements for each run showed excellent agreement between EPA Method 26A and the MEST-H method, generally within 5%–10%. The relative differences (RDs) for the paired MEST-H traps were generally less than 20% RD, with much of the data showing less than 10% RD. Relative accuracy less than 5%.

Redesign of trap and material selection has reduced background contributions of HCl from the sorbent material by a factor of over 10. Blank values are ~100 times lower than the MATS limit for new/reconstructed coal-fired units.

Comparative results between the MEST-M and M29 for Sb, As, Be, and Co show general agreement, and the difference is primarily due to M29 having a higher detection limit than MEST-M. Measured Sb, As, Be, and Co levels were relatively low at both units, with values at or below M29 detection limits. The MEST-M for these metals showed improved detection limits generally of a factor of 2 better than M29 resulting in concentrations that were approximately 50% of M29 detection values.

As seen at other plants, Cd, Cr, Pb, Mn, and Ni were shown to be much more variable, making comparison between MEST-M and M29 difficult. Measured values between the two methods were generally within 100%, with many of the values being within 50%. While precautions were taken to minimize trap Pb and Cd contamination, background contributions were still significant. Cr and Ni showed improved comparative results compared to previously sampled plants. Comparatively, Mn values improved significantly with respect to previous measurements. Hg and Se showed comparable results for both MEST-M and M29 for both units, generally within 20%.

It is extremely difficult, if not impossible, to ensure MATS compliance measurement for all 11 of the trace elements using either M29 or the MEST-M method at the low level concentrations required by MATS. The two main reasons are high background values (Cr, Pb, Mn, and Ni) and limitations of instrumentation detection limits (Sb, As, Be, Cd, and Co). Longer sampling duration and larger sample volumes can improve the method detection proportionally but at the expense of increased time (cost) and risk.

Based on these data and conclusions from previous tests, The MEST-H method shows promise as an alternative to EPA Method 26 or 26A for measuring HCl at the limits for both existing and new/reconstructed coal-fired units.

For the MEST-M method, additional research is still needed to explore possible longer sampling durations and/or selection of lower-background materials before the MEST-M method can be considered as a potential alternative method to Method 29.

This subtask was funded through the EERC–U.S. Department of Energy Joint Program on Research and Development for Fossil Energy-Related Resources Cooperative Agreement No. DE-FC26-08NT43291. Nonfederal funding was provided by the Electric Power Research Institute, the Illinois Clean Coal Institute, Southern Illinois Power Company, and the Center for Air Toxic Metals Affiliates Program.

SUBTASK 4.27 – EVALUATION OF THE MULTIELEMENT SORBENT TRAP (MEST) METHOD AT AN ILLINOIS COAL-FIRED PLANT

OBJECTIVES

The overall goal of this project was to evaluate the applicability and performance of the multielement sorbent trap (MEST) method for measuring trace metal (MEST-M) and hydrochloric acid (HCl, MEST-H) emissions at two power plant units that burn Illinois Basin coal. Specific objectives of the project were as follows:

- To evaluate the applicability and performance of the MEST-M and MEST-H methods in a full-scale field test situation.
- To improve the MEST methods.
- To evaluate the equivalency of the two MEST methods with the corresponding U.S. Environmental Protection Agency (EPA) reference methods.
- To provide metal and HCl stack emission data that can be used by the power plant operators to identify strategies to comply with the Mercury and Air Toxics Standards (MATS).

The ultimate goal of the Energy & Environmental Research Center (EERC) effort, which is ongoing, is to develop, publish, and obtain regulatory acceptance of sorbent trap-based multielement- and/or total halogen-sampling methods, complete with laboratory analysis procedures. The methods should achieve detection limits equivalent to or lower than EPA Methods 29 and 26A and low enough to accurately measure the target hazardous air pollutants (HAPs) at the MATS limits as shown in Appendix A Tables A-1 and A-2 for both existing and new or reconstructed plants.

In order to achieve the goals and objective of this project, the following activities were performed:

- Stack sampling was conducted at two power plant units firing Illinois Basin bituminous coal. Sampling included EPA Method 29, EPA Method 26A, the MEST-M method, and the MEST-H method.
- Coal samples were collected, ultimate–proximate analysis was performed, and each coal sample was analyzed for trace metals and halogens.
- Quality assurance/quality control (QA/QC) measures were defined, and the data collected were evaluated based on those measures.

The results of MEST-M sampling at each unit were compared to EPA Method 29 data, and the results of MEST-H sampling were compared to EPA Method 26A data.

INTRODUCTION AND BACKGROUND

The adequacy of test methods for measuring HAPs from stationary sources has become an increasingly important issue as the levels of pollutants that facilities are permitted to emit decrease. This report presents the results of field tests of a newly developed method for measuring emissions of two classes of HAPs: acid gases (specifically, HCl) and trace metals.

The objective of this research is to develop new methods for measurement of HCl and HAP metals that can be performed more easily, in a shorter time frame, and with equivalent or better accuracy and precision than current stationary source stack test methods. This report includes the results of field tests at two Illinois Basin coal-fired power plant units. These tests are part of a larger program of method development and validation under way at the EERC of the University of North Dakota. The tests were performed with the support of the Illinois Clean Coal Institute and other project participants.

Over the past two decades, emissions of mercury, nonmercury metals, and acid gases from energy generation have become the focus of regulatory rule making. On February 16, 2012, EPA promulgated MATS to reduce mercury, nonmercury metals, and HCl emissions from coal-fired power plants (1). The standard sets limits on mercury, nonmercury metals, and acid gas HCl and, for oil units, hydrofluoric acid emissions from new and existing coal- and oil-fired power plant units. After the compliance deadline (2015, or later if a waiver is given), existing coal- and oil-fired EGUs will have to measure and report emissions and maintain emissions below specified limits. Newly constructed or reconstructed units will have to comply with new/reconstructed unit limits, which are considerably lower than the limits for existing units.

Some coal-fired units may monitor sulfur dioxide (SO_2) as a surrogate for HCl emissions. MATS allows for several alternative standards for nonmercury metals:

- Limits on metal emissions using particulate matter as a surrogate
- Individual nonmercury metals
- Total nonmercury metals

The nonmercury metals that are included in the second and third alternative standard are antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), lead (Pb), manganese (Mn), nickel (Ni), and selenium (Se).

Owners and operators of fired electric generating units (EGUs) may select from any of the above three alternatives but must demonstrate compliance with required limits either using continuous emission monitor (CEM) systems or frequent sampling using EPA-approved reference methods. For units that elect to use CEMs, the CEMs must be certified and validated using EPA-approved reference sampling methods. For coal-fired units that elect to comply with the total or individual nonmercury metal emissions, the unit must conduct metal emission testing every 3 months using EPA Method 29. Likewise, units that do not qualify for SO_2 surrogacy and elect not to use an HCl CEM must conduct HCl emission testing every 3 months using EPA Method 26 or 26A.

As a potential alternative to EPA Methods 29 and 26/26A, the EERC developed an MEST method with two separate sampling applications: one for metals (MEST-M) and one for halogens (MEST-H). The principal difference between the two is the sorbent used in the sampling apparatus. The focus of the current research was on HCl and the HAP metals included in the MATS alternate limits. While the comparative and validation efforts focused on measurement of HCl, measurement data suggest that the MEST-H method can also be used for measurement of hydrogen bromide (HBr). However, since the focus was on validation of HCl and not HBr, results for HBr which are presented in the appendices to this report should be viewed as semiquantitative.

EXPERIMENTAL PROCEDURES

In this study, novel sorbent trap methods developed by the EERC were compared to the results of the standard EPA source test methods. This section describes the sampling procedures and analytical methods used in the test program. The sampling methods and procedures are discussed in more detail in Appendix B.

Concerns with using EPA Methods 26/26A and 29 to meet the MATS requirements include the following:

- Both methods are difficult to use, require highly trained personnel, and involve substantial preparation.
- Both methods require the use of toxic chemicals, creating issues for worker safety, shipping, and disposal.
- A very high level of quality control is required, not only for the sample analysis, but also for the sampling activities.
- The detection limits for EPA Method 29 may not be adequate, in some cases, to measure accurately at the existing unit limits established under MATS. Several of the new unit limits (e.g., As, Be, and Cd for coal and new continental liquid oil units) are well below the capabilities of EPA Method 29 (2, 3).

One of the primary ongoing concerns and challenges of MEST-M is to obtain ultralow blank values for the sorbent and plug materials. Because the amount of each trace element captured during sampling is very small, the blank values need to be as close to zero as possible. Under a previous project, improvements were made to lower blank values (4). By making these improvements and extending the sampling time under this project, it was hoped that background concentrations would be easily distinguishable from measured concentrations. While extending the sampling time did appear to help separate background from measured values, there continue to be some problematic elements (Cd, Cr, Pb, Mn, and Ni), which are discussed below. As a result, the EERC has identified a synthetic material that shows promise to lower background contributions by an order of 10–100, as shown in Figures 1 and 2. Evaluation of this material as a trap material is needed to determine its efficacy to capture MATS metals of interest.

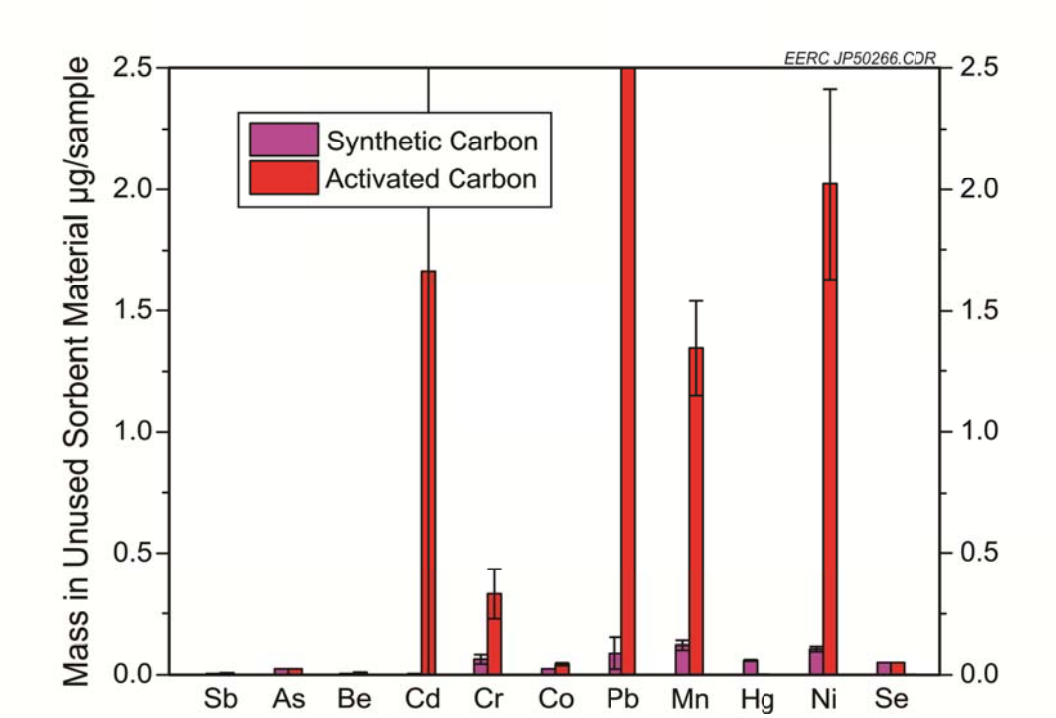

Figure 1. Background concentrations of metals in existing and improved trap material.

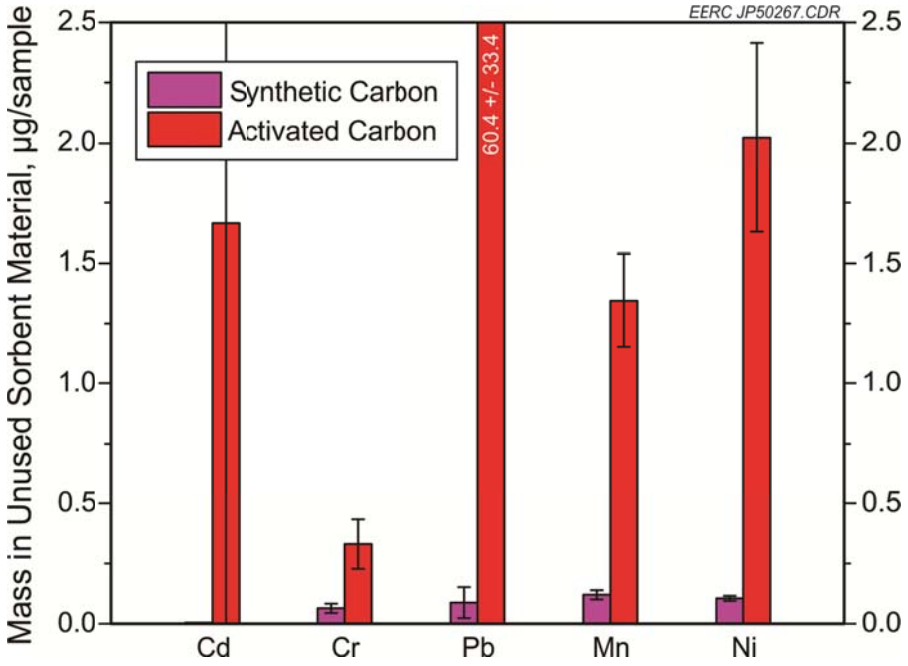

Figure 2. Expanded view of background concentrations for problematic metals (Cd, Cr, Pb, Mn, and Ni).

Halogen Analysis

Analysis of the samples from the MEST-H method was completed for HCl and HBr using ion chromatography (IC). In this project, the analysis was conducted at an off-site laboratory; however, this method is amenable to on-site analysis with appropriate measures to maintain a clean environment. Prior to analysis, the halogens collected by the trap are removed by rinsing the sorbent material and glass wool plugs with high-purity, deionized water. In this way, all halogens from the MEST-H trap are in solution. A calibration curve and baseline are established for the ion chromatograph, the sample is injected into the ion chromatograph, and the peak for each halide ion of interest is determined. The concentration in the injected sample is then calculated based on the calibration curve. The stack emission is calculated from the liquid concentration; the dilution factor (if any); and the stack gas, temperature, gas composition, and volume sampled.

The stack emission detection limit for the MEST-H method is estimated to be 0.01 ppmv on a dry basis, based on the volume of flue gas sampled for this project (250 L). This detection limit was determined based on matrix-matched standards. Comparing this detection limit with the MATS limits in Appendix A-1, the analytical instrumentation appears to be capable of providing adequate sensitivity to detect HCl well below the MATS limits for both existing and new/reconstructed coal-fired units. However, a limit of quantitation (LOQ) has not yet been determined for the MEST-H method. Typically, the LOQ is at least 2.5 times higher than the detection limit, and for a method to be sufficiently accurate for compliance testing, the regulatory limit needs to be higher than the LOQ (5).

Metals Analysis

The following methods were employed for the preparation and analysis of the different samples:

- EPA Method SW846 3052 – Microwave-Assisted Acid Digestion of Siliceous and Organically Based Matrices and SW-846 6020A (inductively coupled plasma–mass spectrometry [ICP–MS]).

- ASTM Method D6357 – Standard Test Methods for Determination of Trace Elements in Coal, Coke, and Combustion Residues from Coal Utilization Processes by ICP–atomic emission spectroscopy (AES), ICP–MS, and graphite furnace atomic absorption spectroscopy (GFAAS).

- ASTM Method D6414 – Standard Test Methods for the Determination of Total Mercury in Coal and Coal Combustion Residues by Acid Extraction or Wet Oxidation/Cold Vapor Atomic Absorption.

Samples from both EPA Method 29 and the MEST-M method are analyzed with ICP–MS for the nonmercury metals. Hg analysis is done separately with cold-vapor atomic absorption spectroscopy (CVAAS). ICP–MS is the preferred analytical method because of its ability to analyze for all of the metals with the lowest detection limits. CVAAS is the preferred method for

Hg analysis because of its selectivity, resulting from the removal of interferents during the cold-vapor generation process as well as the sensitivity of atomic absorption for Hg. The detection limits of ICP–MS for metals are shown in Table 1 along with the detection limit for Hg via CVAAS. The EERC CVAAS instrument/laboratory detection limit of 0.01 μg/L for Hg is significantly lower than that required for the MATS emission limits for existing coal-fired units. This shows that the analytical instrumentation is capable of providing adequate detection levels to measure Hg at the levels required by MATS.

Although the detection limits for the ICP–MS method are such that it appears it can be used to meet the required MATS emission limits for individual trace metals for existing units, the emission limits for several of the metals are at or near the detection limit for ICP–MS. As a result, the precision of the analysis is not very good, as method precision always becomes much worse as the detection limit is approached. For a new or reconstructed unit, method sensitivity becomes more problematic. Hg was not included in this background study, as the instrumental detection limit is a factor of 1000 less than that required for the MATS limit and previous work has reduced background levels to near zero (6).

The estimated MDLs (method detection limits) shown in Table 1 do not take into account sampling variability or background blanks, which can be significant at these levels for several of the metals. In addition, a LOQ has not yet been determined for the MEST-M method; for a method to be sufficiently accurate for compliance testing, the regulatory limit needs to be higher than the LOQ.

Table 1. Estimated Detection Limits of EPA Method 29 and MEST-M Methods

Element	ICP–MS Detection Limit, μg/L	Theoretical EPA Method 29 Detection Limit,[a] μg/dNm^3	Theoretical MEST-M Detection Limit,[b] μg/dNm^3
Antimony	0.1	0.1	0.05
Arsenic	0.5	0.5	0.3
Beryllium	0.1	0.1	0.05
Cadmium	0.1	0.1	0.05
Chromium	0.1	0.1	0.05
Cobalt	0.5	0.5	0.3
Lead	0.1	0.1	0.05
Manganese	0.1	0.1	0.05
Mercury[c]	0.01	0.01	0.005
Nickel	0.2	0.2	0.1
Selenium	1	1	0.5

[a] Based on recovery and dilution volumes, with a sample volume of 1 dNm^3.
[b] Based on recovery and dilution volumes, with a sample volume of 0.25 dNm^3.
[c] CVAAS.

Experimental Approach

Sampling activities for both halogens and metals were performed over the course of 1 week, with sampling activities done simultaneously, as shown in Figure 3. The sampling probe depth was the same for each test method to ensure that the methods were sampling similar and representative flue gas. Sampling at each unit was as follows:

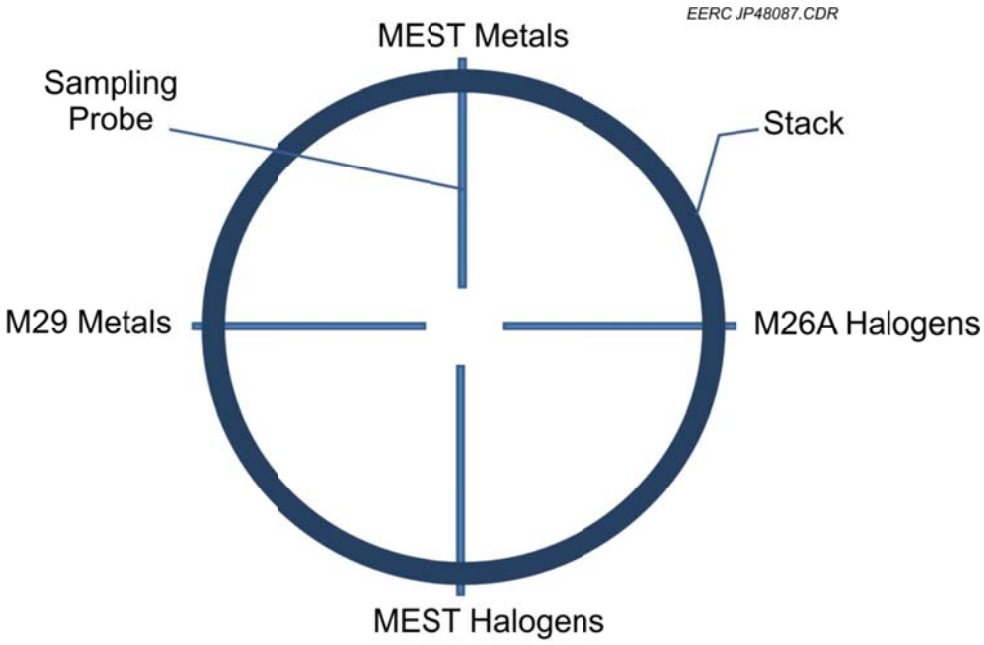

Figure 3. Stack-sampling configuration.

Unit 1

- Ten paired HCl samples of MEST-H were collected along with M26A (nonisokinetic). Four paired metal samples of MEST-M were collected along with M29.
- HCl sampling was of 30-minute duration.
- Metals sampling was of 4-hour duration.

Unit 2

- Four paired HCl samples of MEST-H were collected along with M26A. Ten paired metal samples of MEST-M were collected along with M29.
- HCl sampling was of 90-minute duration.
- Metals sampling was of 4-hour duration.

Although all data are reported, statistical comparisons were only made for valid samples. If one method produced invalid results, then results from both methods were omitted from the statistical evaluation. This will be discussed in more detail later in this report.

The EPA Method 29, MEST-M, and coal samples were analyzed for the trace metals specifically listed in the MATS rule (Sb, As, Be, Cd, Cr, Co, Pb, Mn, Hg, Ni, and Se). EPA Method 26A and MEST-H samples were analyzed for halogens. HCl results (measured as chloride) are reported for the MEST-H method. As stated earlier, HBr results are also reported but should be viewed as preliminary.

The EPA Method 29 and 26A samples were recovered on-site in a laboratory trailer. Once the test team returned to the EERC, all samples were submitted to the EERC's Analytical Research Laboratory (ARL) for preparation and analysis. In the ARL, the MEST-M and EPA Method 29 samples (including filters and plugs) were recovered and prepared for ICP–MS analysis by microwave digestion. MEST-H and EPA Method 26 samples were recovered and prepared for IC analysis.

Description of Power Plants Units and Coals

The two power plant units sampled included a variety of emission control equipment covering a range of stack conditions that challenged the methods. An illustration showing the configurations and sampling location is provided for each unit (Figures 4 and 5).

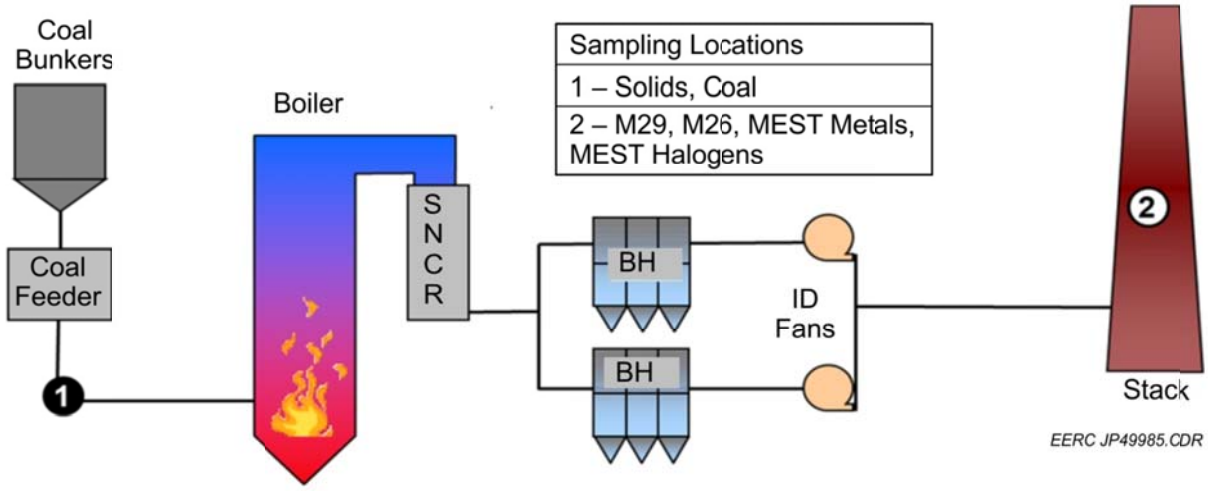

Figure 4. Configuration of Unit 1.

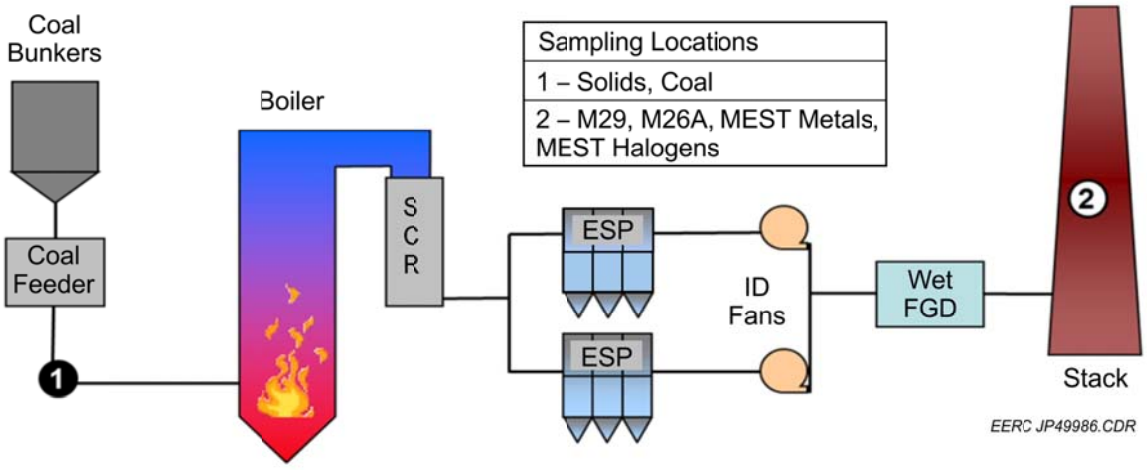

Figure 5. Configuration of Unit 2.

Unit 1 Description

Unit 1 is equipped with a circulating fluidized bed (CFB) and a selective noncatalytic reduction reactor (SNCR) for NO_x control. Particulate matter is controlled by baghouses. Sulfur emissions are controlled by limestone feed to the CFB. The temperature of the flue gas in the stack during sampling ranged from 340° to 360°F. The unit configuration is shown in Figure 4.

Unit 2 Description

Unit 2 is equipped with a pulverized coal (pc) boiler and a selective catalytic reduction reactor (SCR) for NO_x control. Particulate matter is controlled by electrostatic precipitators (ESPs). Sulfur emissions are controlled by a wet flue gas desulfurization (WFGD) scrubber. The temperature of the flue gas in the stack during sampling ranged from approximately 130° to 140°F. The unit configuration is shown in Figure 5.

Coals

Both units burn an Illinois Basin bituminous coal. Coal sample results during sampling activities for each unit are presented in Table 2, including ultimate, proximate, halogen, and trace metal analyses.

RESULTS AND DISCUSSION

This section presents the results of the tests conducted at the two Illinois Basin coal-fired power plant units, summarizes the principal findings of the study, and presents the results of a statistical analysis of a comparison between the results of the EPA standard methods and the sorbent trap (MEST) method.

Table 2. Coal Analyses

Coal	Unit 1		Unit 2	
Sample	Average [a]	Std. Dev.	Average[a]	Std. Dev.
Heating Value, Btu/lb (as-received basis)	9641	206	11,082	103
Proximate Analysis, % as-received				
Moisture, %	13.72	0.90	8.72	0.96
Volatile Matter, %	28.92	0.89	33.96	0.55
Fixed Carbon, %	41.42	0.58	44.85	0.83
Ash, %	15.94	0.71	12.47	1.21
Total	100.00	3.08	100.00	3.55
Coal Analysis, % as-received				
Carbon, %	56.49	1.00	63.15	0.52
Hydrogen, [b] %	3.79	0.08	4.29	0.06
Oxygen in Fuel, [b] %	5.20	1.23	5.75	0.60
Nitrogen, %	1.08	0.04	1.27	0.02
Sulfur, %	3.78	0.15	4.35	0.31
Moisture, %	13.72	0.90	8.72	0.96
Ash, %	15.94	0.71	12.47	1.21
Halogens (ppm dry basis)				
Chlorine, ppmd	789	144	1,195	90.7
Fluorine, ppmd	131	11.3	87.0	4.2
Bromine, ppmd	77	13.2	258	55.4
Trace Element Concentration, ppm in coal, dry basis				
Antimony	0.428	0.052	0.295	0.060
Arsenic	6.413	0.746	5.480	0.762
Beryllium	1.928	0.067	1.903	0.170
Cadmium	1.050	0.146	0.448	0.171
Chromium	20.25	0.968	14.85	0.379
Cobalt	6.358	0.400	4.825	0.318
Lead	26.33	2.701	34.40	3.592
Manganese	64.38	3.092	42.03	7.596
Mercury	0.090	0.004	0.087	0.007
Nickel	14.33	0.680	10.35	0.265
Selenium	2.615	0.097	2.488	0.309

[a] Average of four samples.
[b] Moisture not included for hydrogen and oxygen.

Trace Metal Results

It is extremely difficult, if not impossible, to ensure MATS compliance measurement for all 11 of the trace elements using either M29 (EPA Method 29) or the MEST-M method at the low-level concentrations required by MATS. The two main reasons are high background values (Cr, Pb, Mn, and Ni) and limitations of instrumentation detection limits (Sb, As, Be, Cd, and Co). Longer sampling duration and larger sample volumes can improve the method detection proportionally but at the expense of increased time (cost) and risk. For M29, a potential risk is that the flue gas components will overwhelm the impinger solutions and result in a loss of sample integrity. The sampling duration for this evaluation was extended to 4 hours.

The MEST-M method has been shown to have advantages over M29, with lower detection limits for all of the trace elements under consideration, but similar issues exist with high background values (Cd, Cr, Pb, Mn, and Ni) and limitations of instrumentation detection limits (As, Be, Cd, Sb, and Co) that can be achieved, which are generally at or above the extremely low values as defined for new source limits under MATS.

Unit 1 Results

The average results for the EPA Method 29 and MEST-M sampling methods are presented in Table 3. Note, this table includes only data that are considered valid; a complete data set is provided in Appendix C. A summary of the average metal results for Unit 1 is shown in Figure 6. The error bars on each column indicate the RSDs of the replicate tests. The horizontal lines indicate the MATS limits for existing coal-fired power plant units.

Four sets of data for each sampling method were taken at Unit 1, with results shown in Table 3. The last row in Table 3 shows the relative comparison between the values obtained using M29 and MEST-M. Comparative results between the MEST-M and M29 for Sb, As, Be, and Co show general agreement, and the difference is primarily due to M29 having a higher detection limit than MEST-M. Detection limits were generally lower for the MEST-M method than for EPA Method 29 for these metals. Sb, As, Be, Cd, and Co were measured to be relatively low at both units, with values at or below M29 detection limits. The MEST-M for these metals showed improved detection limits of generally a factor of 2 better than M29, resulting in concentrations that were approximately 50% of M29 detection values.

As shown at other plants, Cr, Pb, Mn, and Ni are generally much more variable, making comparison between MEST-M and M29 difficult. As can be seen in Figure 6, for these metals, measured values between the two methods were generally within 100%, with many of the values being within 50%. While precautions were taken to minimize trap contamination, clearly Pb and Cd background in the trap material were extremely variable and contributed significantly to measurement variability. Cr and Ni showed improved comparative results compared to previous sampled plants, likely because of relatively high concentrations and longer sampling duration. Comparatively, Mn values improved significantly with respect to previous measurements, with

Table 3. Comparison of Metals Measured Between the MEST-M and EPA M29 Methods for Unit 1

		Sb	As	Be	Cd	Cr	Co	Pb	Mn	Hg	Ni	Se
U1 M29-1	lb/TBtu	0.2	1.47	0.465		6.64	1.62	8.6	15.7	0.055	4.54	0.99
U1 M29-2	lb/TBtu	0.1	1.38	0.512	0.330	5.55	1.48			0.034	3.53	0.00
U1 M29-3	lb/TBtu	0.1	1.27	0.506	0.406	5.73	1.58		16.6	0.046	3.63	0.91
U1 M29-4	lb/TBtu	0.2	1.22	0.494	0.364	5.59	1.50	8.4	16.2	0.052	3.32	0.82
Average	lb/TBtu	0.2	1.33	0.494	0.366	5.88	1.54	8.5	16.2	0.047	3.75	0.68
Std. Dev.	lb/TBtu		0.11	0.021	0.038	0.51	0.07	0.2	0.5	0.009	0.54	0.46
RSD	%		8	4	10	9	4	2	3	20	14	68
U1 TM-1	lb/TBtu	0.058	0.62	0.165		7.50	0.89	0.3	23.3	0.035	8.20	0.64
U1 TM-2	lb/TBtu	0.042	0.52	0.200	5.30	5.98	0.70			0.029	4.10	
U1 TM-3	lb/TBtu	0.046	0.40	0.126	9.20	7.52	0.77		22.8	0.037	3.64	0.86
U1TM-4	lb/TBtu	0.044	0.40	0.166	3.31	8.10	0.68	74.4	23.3	0.031	3.17	0.37
Average	lb/TBtu	0.048	0.48	0.164	5.97	7.28	0.76	37.4	23.1	0.033	4.76	0.62
Std. Dev.	lb/TBtu	0.007	0.11	0.030	3.01	0.90	0.10	52.4	0.30	0.004	2.30	0.24
RSD	%	15	22	18	51	12	13	140	1	11	48	39
Average Diff.*	%	−69	−64	−67	1528	24	−51	341	43	−29	27	−8

* Percentage difference between MEST-M and M29 average values (MEST-M-M29)/M29.

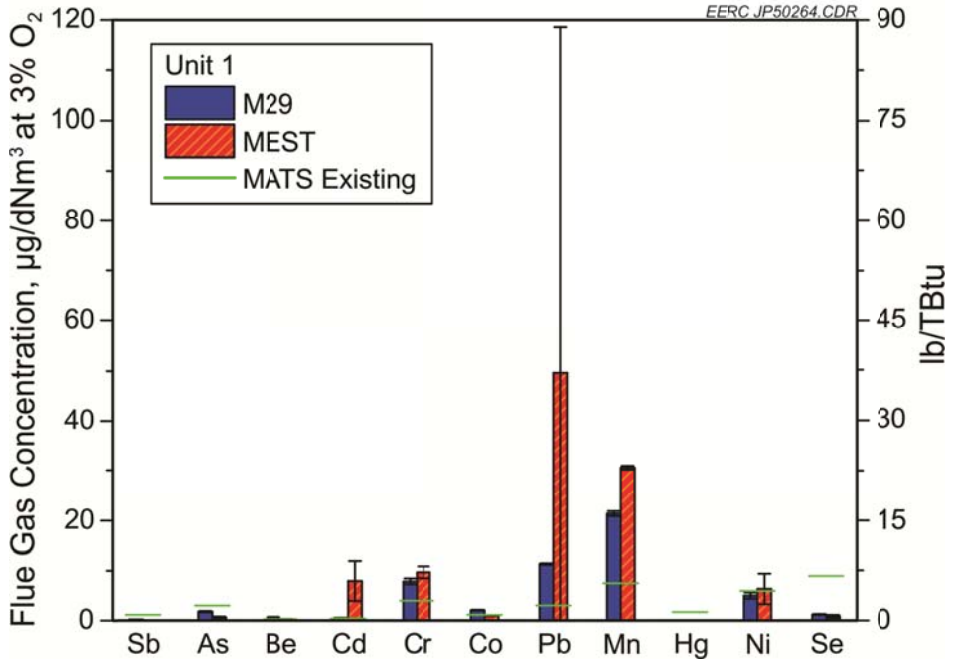

Figure 6. Comparison of EPA Method 29 and MEST-M Averages for Unit 1.

measurement generally within 50%. Hg and Se showed comparable results for both MEST-M and M29, generally within 20%. Note, for Unit 1, Hg was below the reliable detection limit for M29. Results for each element are graphically presented in Appendix D.

Metal concentrations in the coal were compared to measured stack emissions for each method to determine the capture of the metals in the bottom ash, ESPs, and WFGD prior to the stack. These results are summarized in Table 4, which shows that the capture of all (except Hg and Se) metals was greater than 98%–99%. Where either method had results below detection limits, the detection limit was used to calculate capture efficiency. While all of the metals had a removal efficiency of greater than 99%, the emissions for many were still above the individual MATS limits, as highlighted in Table 4.

Unit 2 Results

The average results for the EPA Method 29 and MEST-M sampling methods are presented in Table 5. This table includes only results that are valid according to project data acceptance criteria; a complete data set is provided in Appendix C. A column plot showing the average metal results for Unit 2 is shown in Figure 6. The error bars on each column indicate the RSDs of the replicate tests. The horizontal lines indicate the MATS limits (converted to $\mu g/Nm^3$) for existing Illinois bituminous coal-fired power plant units.

Ten sets of data for each sampling method were taken at Unit 2, with results shown in Table 6. The last row in Table 6 shows the relative comparison between the values obtained using M29 and MEST-M. Comparative results between the MEST-M and M29 for Sb, As, Be, and Co show general agreement, and the difference is primarily due to M29 having a higher detection limit than MEST-M. Detection limits were generally lower for the MEST-M method than for EPA Method 29 for these metals. Sb, As, Be, and Co were measured to be relatively low at both units, with values at or below M29 detection limits. The MEST-M for these metals showed improved detection limits of generally a factor of 2 better than M29, resulting in concentrations that were approximately 50% of M29 detection values.

As shown at other plants, Cr, Pb, Mn, and Ni are generally much more variable, making comparison between MEST-M and M29 difficult. As can be seen in Figure 7, for these metals, measured values between the two methods were generally within 100%, with many of the values being within 50%. While precautions were taken to minimize trap contamination, clearly Pb and Cd backgrounds in the trap material were extremely variable and contributed significantly to measurement variability. Cr and Ni showed improved comparative results compared to previously sampled plants, likely due to relatively high concentrations and longer sampling duration. Comparatively, Mn values improved significantly with respect to previous measurements, with measurement generally with 50%. Hg and Se showed comparable results for both MEST-M and M29, generally within 20%. Results for each element are graphically presented in Appendix D.

Table 4. Trace Metal Capture at Unit 1 Using EPA Method 29 and the MEST-M Sampling Method*

Method 29												
		Sb	As	Be	Cd	Cr	Co	Pb	Mn	Hg	Ni	Se
Average Stack Emissions**	lb/TBtu	0.2	1.33	0.494	0.366	5.88	1.54	8.5	16.2	0.051	3.75	0.68
MATS Limit	lb/TBtu	0.8	1.1	0.2	0.3	2.8	0.8	1.2	4.0	1.2	3.5	5.0
Average in Coal	lb/TBtu	38	575	173	94.1	1810	570	2360	5760	8.10	1280	234
Required Removal to Meet MATS	%	97.91	99.81	99.88	99.68	99.85	99.86	99.95	99.93	85.18	99.73	97.86
Removed	%	99.48	99.77	99.71	99.61	99.68	99.73	99.64	99.72	99.37	99.71	99.71
Method MEST-M												
		Sb	As	Be	Cd	Cr	Co	Pb	Mn	Hg	Ni	Se
Average Stack Emissions**	lb/TBtu	0.048	0.482	0.164	9.24	7.28	0.761	37.4	23.1	0.033	4.76	0.624
MATS Limit	lb/TBtu	0.8	1.1	0.2	0.3	2.8	0.8	1.2	4.0	1.2	3.5	5.0
Average in Coal	lb/TBtu	38	575	173	94.1	1810	570	2360	5760	8.10	1280	234
Required Removal to Meet MATS	%	97.91	99.81	99.88	99.68	99.85	99.86	99.95	99.93	85.18	99.73	97.86
Removed	%	99.88	99.92	99.90	90.18	99.60	99.87	98.42	99.60	99.59	99.63	99.73

* Highlighted cell indicates average emission reduction would not be sufficient to achieve individual metal MATS limit for existing units.

** Average value after applying data acceptance criteria.

Table 5. Comparison of Metals Measured Between the MEST-M and EPA M29 Methods for Unit 2

		Sb	As	Be	Cd	Cr	Co	Pb	Mn	Hg	Ni	Se
U2 M29-1	lb/TBtu	0.2	3.40	0.107		42.7				0.59	26.1	26.3
U2 M29-2	lb/TBtu	0.229	3.15	0.030	0.098	47.1		3.26		0.52		34.4
U2 M29-3	lb/TBtu	0.2	3.11	0.040	0.227	65.2		4.54	19.3	0.63		26.5
U2 M29-4	lb/TBtu	0.2	3.33	0.034	0.111	55.0	0.590			0.70		21.2
U2 M29-5	lb/TBtu	0.2	3.37	0.046		38.6	0.472		25.6	0.57	20.0	30.3
U2 M29-6	lb/TBtu	0.2	3.37	0.042		79.0	0.703		19.0	1.03	40.9	29.3
U2 M29-7	lb/TBtu	0.2	2.86	0.055		38.5	0.610		17.0	0.51	22.1	31.1
U2 M29-8	lb/TBtu	0.2	3.28	0.110		27.0	0.490		18.1	0.85	16.7	31.6
U2 M29-9	lb/TBtu		2.62	0.053						0.90		48.1
U2 M29-10	lb/TBtu	0.2	2.45	0.052	0.160	29.7	0.370		15.7	0.80	19.8	35.4
Average	lb/TBtu	0.2	3.09	0.057	0.150	47.0	0.540	3.90	19.1	0.71	24.3	31.4
Std. Dev.	lb/TBtu		0.34	0.028	0.060	16.8	0.120	0.90	3.4	0.18	8.70	7.2
RSD	%		11	48	39	36	22	23	18	25	36	23
U2 TM-1	lb/TBtu	0.021	1.72	0.039		5.81				0.61	3.75	31.4
U2 TM-2	lb/TBtu	0.024	1.81	0.044	0.695	7.70		23.9		0.58		37.8
U2 TM-3	lb/TBtu	0.059	1.59	0.050	0.010	2.73		0.356	13.8	0.64		37.6
U2 TM-4	lb/TBtu	0.102	1.72	0.040	0.043	12.5	0.230			0.75		38.8
U2 TM-5	lb/TBtu	0.057	2.24	0.049		9.20	0.240		18.0	0.65	4.07	34.3
U2 TM-6	lb/TBtu	0.026	1.67	0.030		7.50	0.240		20.7	1.16	13.0	28.7
U2 TM-7	lb/TBtu	0.048	1.84	0.043		12.5	0.170		19.6	0.63	2.23	34.3
U2 TM-8	lb/TBtu	0.041	1.54	0.040		6.78	0.142		18.5	0.88	1.64	34.2
U2 TM-9	lb/TBtu		0.84	0.019						0.80		29.0
U2 TM-10	lb/TBtu	0.034	1.12	0.037	1.21	4.32	0.161		16.1	0.86	1.16	33.5
Average	lb/TBtu	0.046	1.61	0.039	0.490	7.68	0.198	12.1	17.8	0.76	4.31	34.0
Std. Dev.	lb/TBtu	0.025	0.39	0.009	0.576	3.35	0.045	16.6	2.49	0.18	4.40	3.50
RSD	%	55	24	23	117	44	23	137	14	23	102	10
Average Diff. *	%	−78	−48	−31	228	−84	−63	211	−7	7	−82	8

* Percentage difference between MEST-M and M29 average values (MEST-M-M29)/M29.

Table 6. Trace Metal Capture at Unit 2 Using EPA Method 29 and the MEST-M Sampling Method*

		Method 29										
		Sb	As	Be	Cd	Cr	Co	Pb	Mn	Hg	Ni	Se
Average Stack Emissions**	lb/TBtu	0.2	3.09	0.051	0.15	43.0	0.54	3.90	19.1	0.71	24.3	31.4
MATS Limit	lb/TBtu	0.8	1.1	0.2	0.3	2.8	0.8	1.2	4.0	1.2	3.5	5.0
Average in Coal	lb/TBtu	24.3	451.8	156.7	36.90	1223.4	397.6	2834.2	3467.5	7.1	852.6	204.9
Required Removal to Meet MATS	%	96.71	99.76	99.87	99.19	99.77	99.80	99.96	99.88	83.17	99.59	97.56
Removed	%	99.18	99.32	99.97	99.60	96.48	99.86	99.86	99.45	90.05	97.15	84.67
		Method MEST-M										
		Sb	As	Be	Cd	Cr	Co	Pb	Mn	Hg	Ni	Se
Average Stack Emissions**	lb/TBtu	0.046	1.61	0.039	0.490	7.68	0.198	12.1	17.8	0.757	4.31	34.0
MATS Limit	lb/TBtu	0.8	1.1	0.2	0.3	2.8	0.8	1.2	4.0	1.2	3.5	5.0
Average in Coal	lb/TBtu	24.3	451.9	156.7	36.9	1223.4	397.6	2834.2	3467.5	7.1	852.7	204.9
Required Removal to Meet MATS	%	96.71	99.76	99.87	99.19	99.77	99.80	99.96	99.88	83.17	99.59	97.56
Removed	%	99.81	99.64	99.98	98.67	99.37	99.95	99.57	99.49	89.39	99.49	83.43

* Highlighted cells indicate average emission reduction would not be sufficient to achieve individual metal MATS limit for existing units.

** Average value after applying data acceptance criteria.

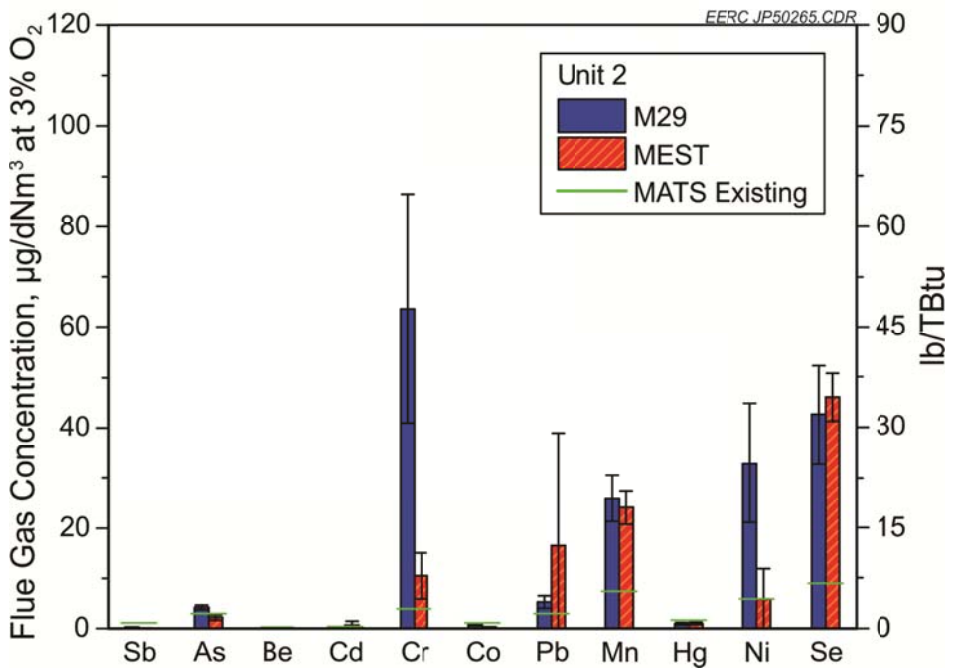

Figure 7. Comparison of EPA Method 29 and MEST-M Data for Unit 2.

Metal concentrations in the coal were compared to measured stack emissions for each method to determine the capture of the metals in the bottom ash, ESPs, and WFGD prior to the stack. These results are summarized in Table 6, which shows that the capture of all metals was greater than 98%–99%. Where either method had results below detection limits, the detection limit was used to calculate capture efficiency. While all of the metals had a removal efficiency of greater than 99%, the emissions for many were still above the individual MATS limits, as highlighted in Table 6.

HCl Results

HCl was measured at each of the two units using EPA Method 26A and MEST-H sorbent traps.

Because both units burned Illinois Basin coal, the coal chlorides were relatively high, averaging greater than 700 and 1200 ppmvd for Units 1 and 2, respectively. However, Unit 1 is equipped with a baghouse and Unit 2 with a scrubber, so the HCl emissions are expected to be relatively low, in comparison to the amount of chlorine in the coal. The average results for each stack test method are shown in Table 7 and Figure 8. The error bars on each column in Figure 8 indicate the RSD of the replicate tests. The results for Unit 1 are significantly above the MATS limit for existing units, whereas for Unit 2, values are near to or slightly below the limit. As shown in Table 7, capture of HCl was approximately 30% at Unit 1 and greater than 98% at Unit 2. The complete results are provided in Appendix E and F.

Table 7. HCl Capture at Units 1 and 2 Using EPA Method 26A and the MEST-H Sampling Method

	Unit 1				Unit 2			
	MEST-H		EPA M26A		MEST-H		EPA M26A	
Sample ID	ppmvd	lb/MMBtu ($\times 10^{-3}$)	ppmvd	lb/MMBtu ($\times 10^{-3}$)	ppmvd	lb/MMBtu ($\times 10^{-3}$)	ppmvd	lb/MMBtu ($\times 10^{-3}$)
1	43.3	49.7	43.7	50.1	1.4	1.6	1.1	1.3
2	45.5	52.2	43.7	53.8	0.9	1.0	0.6	0.7
3	41.7	47.8	42.8	49.2	1.4	1.6	1.7	1.9
4	43.3	49.7	45.1	51.7				
5	42.9	49.2	46.2	53.1				
6	42.0	48.3	44.5	51.1				
7	41.1	47.2	43.3	49.7				
8	43.1	49.5	43.1	49.5				
9	40.5	46.5	42.9	49.2				
10	41.8	48.0	44.1	50.6				
Average	42.5	48.8	44.3	50.8	1.2	1.4	1.2	1.3
Std. Dev.	1.4	1.6	1.4	1.6	0.3	0.3	0.5	0.6
RSD	3.3	3.3	3.2	3.2	24.8	24.8	45.8	45.8
MATS Limit	~1.8	2.0	~1.8	2.0	~1.8	2.0	~1.8	2.0
Average in Coal	63	72.7	63	72.7	90	101.6	90	101.6
Required Removal to Meet MATS Limit		97.25		97.25		98.03		98.03
Removed		32.82		30.07		98.64		98.72

HBr Results

HBr was measured at each of the two units using EPA Method 26A and MEST-H sorbent traps. While the validation efforts to date have focused on measurement of HCl, measurement data suggest that the MEST-H method can also be used to measure HBr. Data in Figure 9 show agreement between M26A and the MEST-H method; however, the agreement was better for the scrubbed unit than for the unit with a baghouse.

The apparent bias of MEST-H over M26A of approximately 40%–50% for Unit 1 may be due to bromine that is retained on the M26A filter, which is not analyzed by the EPA method. Furthermore, the MEST-M may collect some bromine on the glass wool plug, which is analyzed along with the sorbent material. The unburned carbon and particulate emissions from Unit 1 are quite different from Unit 2, resulting in different observed phenomenon. However, it is known that when flue gas that contains ash (relatively high in carbon) collects on a filter, additional bromine will be collected. Other than this bias, the data match and trend very well. The complete results are provided in Appendix E and F.

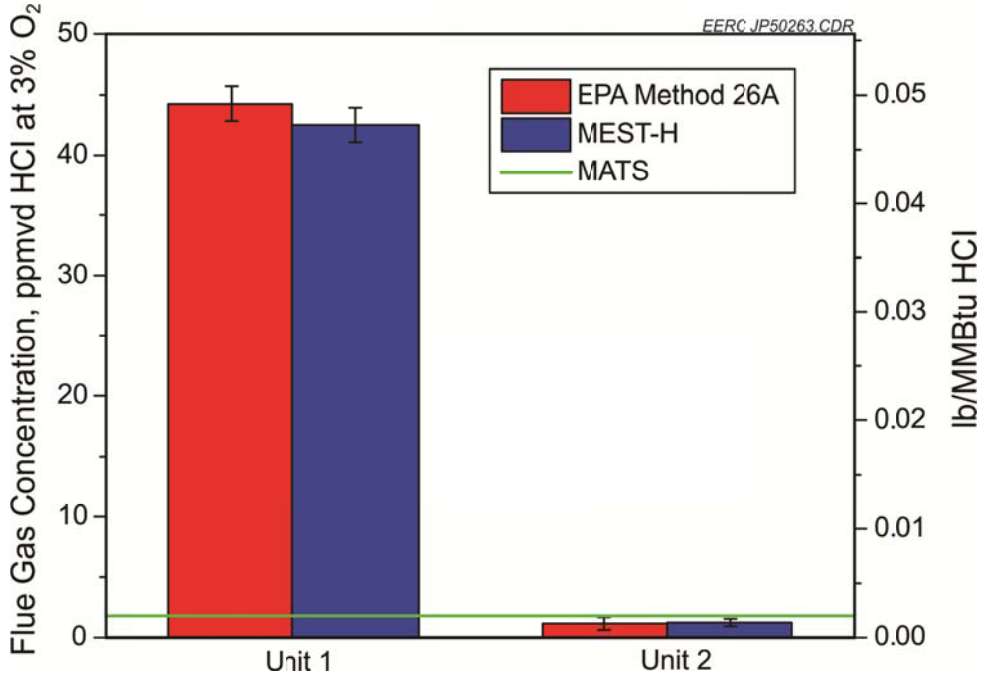

Figure 8. Average flue gas HCl results comparing EPA Method 26A with MEST-H.

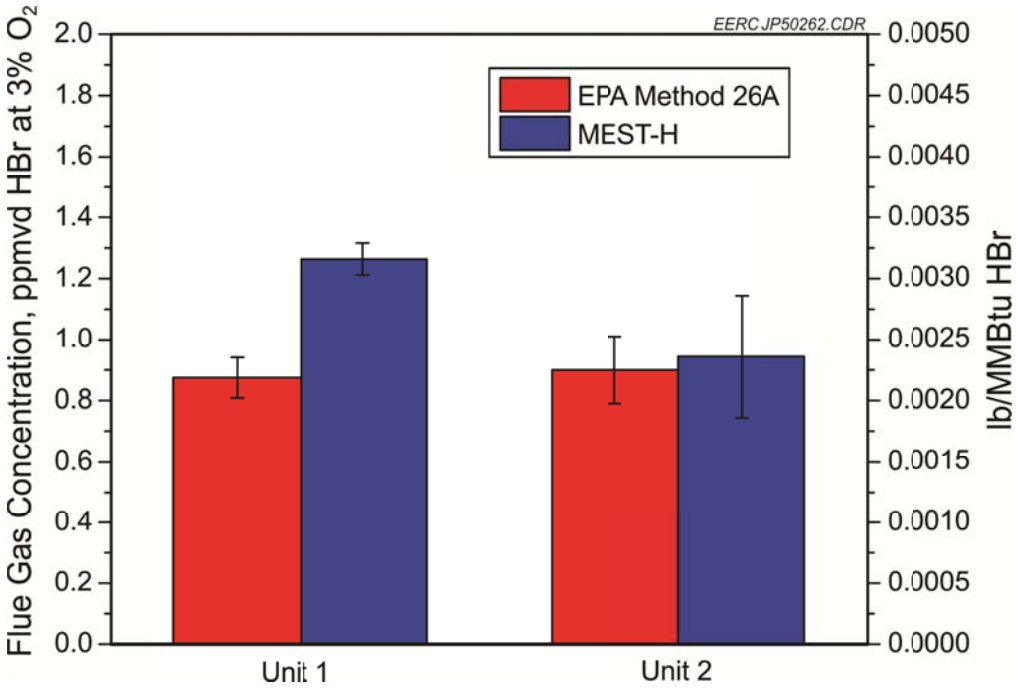

Figure 9. Average flue gas HBr results comparing EPA Method 26A with MEST-H.

Statistical Comparison of MEST and EPA Methods

Although the data sets obtained in this project are too few for a complete EPA Method 301 validation, they were used to statistically compare the MEST method to the EPA reference methods, EPA Methods 29 and 26A. In addition, QA/QC criteria established by EPA Methods 29 and 26A and the MEST method resulted in several invalid samples. As a result, the statistical comparison was made with available valid sets of paired (EPA Methods 29 and 26A and MEST) samples.

The project criteria established for evaluation of accuracy, precision, and bias were as follows:

- A valid statistical comparison between the two sampling methods can only be made if both methods have results above the detection limit and the background (blank) concentrations are ≤30% of the measured value.

- Because concentrations are often at or near the detection limits of one or both of the sampling methods, the blank-corrected concentrations often fall below the detection limits. Only samples where both measurements were above detection limits were included in the statistical analysis.

- For the MEST method, an RD for the paired traps of ≤20% was used for HCl data and ≤50% for metals data. Note, a higher acceptance value was used for metals because of the low measurement concentrations and background variability. As previously discussed, the results for both methods taken simultaneously must be valid for the sample data to be used in the statistical analysis.

- Relative accuracy (RA) was also calculated to determine the degree of relative imprecision between the MEST method and EPA reference methods (RM). An RA of greater than 100% was used as an out-of-bounds (pass/fail) criteria. RA is calculated by the following equation. RA = (average of differences between MEST and RM) * cc/average of RM values.

  While similar to the bias calculation (average difference/average RM), the RA calculation also includes a confidence coefficient (cc), which is a measurement of the uncertainty in the calculation and includes evaluation of the distribution of differences between the MEST and reference methods. The term "cc" is calculated from the standard deviation divided by the square root of number of samples, and applying a t statistic factor.

- Relative bias was calculated using Method 301 procedures using Equation 301-7 and Equation 301-10. The significance of any bias between the methods for any individual trace metal (or halogen) is determined by comparing the calculated t statistic for the number of valid samples analyzed (Equation 301-7) to the t statistic tables for 95% confidence level and the appropriate degrees of freedom. If the calculated bias is ≤10%, then it is insignificant and the two methods are statistically the same. If the bias

is significant (ie., calculated t statistic > the t statistic from the tables), then the actual bias must be calculated. If the bias is >10% but ≤30%, the bias is significant, and consideration would need to be given on whether a bias correction could be applied. A bias of >30% would not be considered acceptable.

- Method precision was calculated based on the variance between the methods for the valid samples. The estimated variance is calculated for the two sampling methods using Equation 301-11 and Equation 301-12. The value from this calculation is then compared to the one-sided F statistic at the 95% confidence level. If the calculated F is outside of this critical range (calculated F statistic > the F statistic from the tables), the difference in precision is significant. If the concentrations were below the detection limit for one or both of the methods, the F calculations cannot be completed, and the methods are deemed equivalent (Eq). If the F statistical analysis can be completed, then the determination of precision is simply pass or fail. "Pass" indicates that the precision of the two methods are statistically comparable; "fail" indicates they are not.

As stated above, a valid statistical comparison between the two sampling methods for valid samples can only be made if both methods have results above the detection limit and the background (field blank) concentrations are ≤30% of the measured value. It should be noted that if the results for both methods are below detection limits, then they must be considered statistically equivalent.

Statistical Comparison of MEST-M and EPA Method 29

It is extremely difficult, if not impossible, to obtain accurate metals measurements for all 11 of the HAPs metals at the low-level concentration limits specified by MATS using either M29 (EPA Method 29) or the MEST-M method. The two main reasons are high background values (Cr, Pb, Mn, and Ni) and limitations of instrumentation detection limits (for Sb, As, Be, Cd, and Co). Longer sampling duration and larger sample volumes can improve the method detection limit proportionally to the volume of flue gas collected but at the expense of increased time (cost) and risk. For M29, a potential risk is that the flue gas components will overwhelm the impinger solutions (changing the pH) and result in a loss of sample integrity. The sampling duration for this evaluation was extended to 4 hours. The statistical calculations and criteria as discussed above were applied and are summarized for both Units 1 and 2 in Table 8.

Statistical Comparison for Unit 1 Metals

For Unit 1, Hg and Se were the only trace metals for which all statistical criteria were met. However, it should be recalled that this data set is rather small (four stack tests). The average values show a bias for both Hg and Se for the MEST-M method compared to M29. It should be noted, however, that the mercury concentration is below the level that EPA M29 can measure reliably. For Hg, the relative bias was significant at the 95% confidence level. The relative bias of EPA Method 29 over the MEST-M method for Hg was calculated to be 29.1%, which is outside the range of 10% to be insignificant but less than the 30% bias that would make the methods not comparable according to EPA Method 301 criteria. The precision of the two

Table 8. Statistical Comparison of the Average Trace Metal Results for EPA Method 29 and the MEST-M Method (all concentrations in µg/dNm^3)

Unit 1	**Sb**	**As**	**Be**	**Cd**	**Cr**	**Co**	**Pb**	**Mn**	**Hg**	**Ni**	**Se**
M29 Average	0.20	1.8	0.65	0.48	7.8	2.0	11	21	0.06	5.0	1.2
MEST-M Average	0.06	0.64	0.22	7.9	9.6	1.0	49	31	0.04	6.3	0.82
n, Valid Data Sets	4	4	4	3	4	4	2	4	4	4	3
t"0.025 Table	3.18	3.18	3.18	4.30	3.18	3.18	12.71	3.18	3.18	3.18	4.30
t Calc. Value	29.63	66.99	18.56	3.25	3.08	35.51	0.8	17.57	3.34	1.14	2.4
RD Avg. %	53.0	47.3	50.3	86.7	10.4	34.1	86.4	17.7	16.3	9.5	20.7
RA %	1.0	3.4	5.0	14990	45.5	4.7	212550	238	0.5	99.6	20.8
Bias %	69.2	63.8	66.8	1528	23.8	50.7	340	32.2	29.1	26.8	31.3
F Calc. Value	0.25	0.90	2.05	6257	3.10	2.12	87194	0.41	0.15	18.0	7.53
F Table Value	6.39	6.39	6.39	9.28	6.39	6.39	19.00	6.39	6.39	6.39	9.28
RA Test	Eq*	Pass	Pass	Fail	Fail	Pass	Fail	Fail	Pass	Pass	Pass
Bias Test	Eq	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Pass	Pass	Pass
F-Test	Eq	Pass	Pass	Fail	Pass	Pass	Fail	Pass	Pass	Fail	Pass
Unit 2	**Sb**	**As**	**Be**	**Cd**	**Cr**	**Co**	**Pb**	**Mn**	**Hg**	**Ni**	**Se**
M29 Average	0.29	4.2	0.08	0.20	64	0.73	5.3	26	0.96	33	43
MEST-M Average	0.06	2.2	0.05	0.66	10	0.27	16	24	1.0	5.8	46
n, Valid Data Sets	9	10	10	4	9	6	2	6	10	6	10
t"0.025 Table	2.31	2.26	2.26	3.18	2.31	2.57	12.71	2.57	2.26	2.57	2.26
t Calc. Value	14.62	17.59	1.90	1.15	6.81	7.98	0.66	0.80	2.33	10.34	0.85
RD Avg. %	65.4	32.5	22.1	71.9	70.3	45.9	80.7	8.0	4.6	74.3	10.4
RA %	2.8	12.4	0.9	290	1505	9.4	44853	42.5	0.4	552	74.5
Bias %	78.4	48.0	31.2	228	83.7	63.2	210	7.1	6.7	82.3	8.1
F Calc. Value	5.32	1.31	0.11	96.5	0.04	0.14	337	0.52	1.00	0.25	0.24
F Table Value	3.18	2.98	2.98	6.39	3.18	4.28	19.0	4.28	2.98	4.28	2.98
RA Test	Eq	Pass	Pass	Fail	Fail	Pass	Fail	Pass	Pass	Fail	Pass
Bias Test	Eq	Fail	Pass	Fail	Fail	Fail	Fail	Pass	Pass	Fail	Pass
F-Test	Eq	Pass	Pass	Fail	Pass	Pass	Fail	Pass	Pass	Pass	Pass

* Equivalent since both averages are below detection limits.

methods for Hg was comparable (pass) based on an F-test. For Se, the relative bias was slightly above 30%, but because the t-statistic calculation resulted in a value less than the t value from statistical tables, the bias is considered insignificant according to M301 criteria.

For Sb, the two methods were determined to be statistically equivalent, as all of the values are below the M29 detection limit, although the detection limit for the MEST-M is approximately 50% lower than M29. The two methods were comparable for As and Co as well, with a relative accuracy below 10%. The two methods showed much more variability for Cr, Ni, and Mn, likely due to varying background concentrations among samples and a limited data set. While precautions were taken to minimize background contribution, the data clearly show that Pb and Cd had highly varying results, suggesting fairly high and varying background concentrations.

Statistical Comparison for Unit 2 Metals

For Unit 2 (ten stack tests), all statistical criteria were met for Hg, Se, Be, and Mn. For Hg, Se, and Mn, the relative bias between the two methods was less than 10%. For Be, although the relative bias was slightly above 30%, the t-statistic calculations resulted in a value less than the t value from statistical tables; therefore, according to M301, the bias is considered insignificant.

For Sb, the two methods were determined to be statistically equivalent as all of the values are below the M29 detection limit, although the detection limit for the MEST-M is approximately 50% lower than M29. The two methods were comparable for As and Co as well, with a relative accuracy of approximately 10%. The two methods showed much more variability for Cr and Ni, likely due to variable sorbent concentrations. While precautions were taken to minimize background contribution, the data clearly show that Pb and Cd had highly variable results, suggesting fairly high and varying background concentrations.

Summary of Statistical Evaluation for Metals

Detection limits had a strong impact on the comparability of the two methods. At both units tested, the MEST-M method had lower detection limits than M29 for all of the trace elements under consideration. However, both methods had similar issues with high background values for Cd, Cr, Pb, Mn, and Ni. For As, Be, Cd, Sb, and Co, detection limits for both methods were generally at or above the MATS limits for new/reconstructed coal units.

At both units, results from the two methods for Sb, As, Be, and Co were in general agreement; differences were primarily due to M29 having a higher detection limits than MEST-M. Sb, As, Be, and Co were measured to be relatively low at both units, with values at or below M29 detection limits. The MEST-M for these metals showed improved detection limits of generally a factor of 2 better than M29, resulting in concentrations that were approximately 50% of M29 detection values.

Results for Cd, Cr, Pb, Mn, and Ni were highly variable among test runs, making comparison between MEST-M and M29 difficult. The two methods were generally within 100% difference, with many of the test runs being within 50%. While precautions were taken to minimize trap contamination, Pb and Cd background in the trap material were extremely variable

and contributed significantly to measurement variability. Cr and Ni showed improved comparative results compared to previously sampled plants, likely due to relatively high concentrations and longer sampling duration. The comparability of the two methods for Mn improved significantly with respect to previous studies, with measurements generally within 50% difference. Hg and Se showed comparable results for both MEST-M and M29 for both units, generally within 20%. For Unit 1, Hg was below the reliable detection limit for M29.

Statistical Comparison of the MEST-H and EPA Method 26A

The statistical procedures used to evaluate the comparability of EPA Method 26A and the MEST-H method were the same as detailed above. The average results and statistical comparisons between the reference method and the MEST-H method are shown in Table 9. It should be noted that for Unit 2 there were only three test runs, which should be kept in mind when reviewing statistical results. Additional samples would add more weight to the statistical results.

At both units, there was no significant bias with the MEST-H method compared to the reference method, and the precision of both methods was very good, as shown in Tables 5 and 6. The variance of the MEST-H paired trap value for Unit 1 was calculated to be 2.02 and 1.98 for EPA Method 26A, resulting in an F value of 1.02, which is less than the one-sided F value of 2.98 for 9 degrees of freedom. The variance of the MEST-H paired trap value for Unit 2 was calculated to be 0.09 and 0.28 for EPA Method 26A, resulting in an F value of 0.33, which is less than the one-sided F value of 9.3 for 2 degrees of freedom. For both units, precision and accuracy requirements were met, suggesting that the MEST-H method for HCl measurement may serve as a good alternative to Method 26A.

Table 9. Average Concentrations and Statistical Analysis of HCl Results for EPA Method 26A and the MEST-H Method

HCl	Unit 1 lb/MMBtu ($\times 10^{-3}$)	Unit 2 lb/MMBtu ($\times 10^{-3}$)
M26A Average	50.8	1.3
MEST-H Average	48.8	1.4*
n, Valid Data Sets	10	3*
t"0.025 Table	2.3	4.3
t Calc. Value	5.3	0.1
RD Avg. %	2.0	3.2
RA %	2.9	5.0
Bias %	3.9	−6.6
F Calc. Value	3.0	9.3
F Table Value	1.0	0.3
RA Test	Pass	Pass
Bias Test	Pass	Pass
F-Test	Pass	Pass

* One of the three sets of paired traps at Unit 2 exceeded the RD acceptance criterion of 20% with a value of 29% but was included in the analysis.

Estimate of Cost and Labor

Both the MEST-M and MEST-H methods can easily be deployed in the field without the use of strong acids, bases, or solvents. In addition, these methods are safer and more flexible than EPA Method 29 or 26/26A, as the sorbent traps can easily be shipped for analysis since multiple sample bottles containing hazardous solvents are not required. The MEST methods are also expected to be substantially less time-consuming and less costly than EPA Method 29 or 26A, based on a cost estimate shown in Table 10. Assumptions that were made for Table 10 are as follows (costs are on a per-sample basis):

- $25/hr for field samplers.
- $30/hr for a chemist.
- $10/metal or halogen analyzed.
- Samples are shipped to an off-site laboratory overnight.
- EPA Method 29 and 26A samples require shipping as hazardous materials.
- 10% replacement cost for EPA Method 29 and 26A glassware per sample.

The costs presented in Table 10 are projected to save a utility plant approximately $50,000/yr when performing quarterly sampling to demonstrate compliance with MATS. Krenzke recently reported a cost per sample to complete a M26A sample of $2000–$2500, which is above what is projected for M26A sampling in Table 10 (7).

Other potential costs that were not quantified in Table 10 are:

- Space for sample storage.
- Space for equipment storage.
- Equipment depreciation.
- Power requirements.

The cost of sample storage is not included but would be higher for the EPA reference methods because of the substantial amount of glassware needed and the resulting potential for glassware breakage.

Table 10. Cost Analysis Comparing the EPA Reference Methods to the MEST Methods

	M29	MEST-M	M26A	MEST-H
Labor, minutes	810	360	570	240
Labor Costs, $	1320	610	930	400
Supplies, $	325	100	210	50
Misc.,[a] $	560	100	450	80
Analysis,[b] $	330	440	20	40
Total, $	2535	1250	1610	570

[a] Shipping samples, sample disposal, disposal of analytical waste, reporting, contingency.
[b] Includes analyses of A and B traps for MEST.

QUALITY ASSURANCE/QUALITY CONTROL

The primary documents guiding QA/QC for this program were the procedures outlined in EPA Methods 29, 26A and, for the MEST methods, EPA Method 30B. For the two wet-chemistry methods, the primary QA/QC focus is on field and method blanks and calibration procedures for the instrumentation (ICP–MS for nonmercury metals, CVAAs for Hg, and IC for halogens). For EPA Method 30B, QC measures include the use of duplicate traps, field blanks, breakthrough requirements, and instrument calibration procedures.

Spiked HCl Traps

Analyses were performed on two sets of spiked traps; the first set were unused traps spiked at a single concentration to obtain variability data. The second set were spiked at a range of concentrations and were used as the "A" trap during field sampling. Traps were recovered in two stages. The first section was spiked with known quantities of chlorides. The front stage was the combination of the Tube Rinse (TR), Plug 1 (P1), Section 1 (S1), and Plug 2 (P2), recovered in ~50 mL of high-purity deionized (DI) water. The back stage was the combination of Section 2 (S2) and Plug 3 (P3) recovered in ~50 mL of DI water. Spike recoveries for the two sets of traps are shown in Tables 11 and 12. Spike recoveries are all within 10% of the expected value, showing an excess recovery averaging about 6%–7%. All of the spike was recovered in the first stage of the traps.

Table 11. First Set of Spiked Unused MEST-H Traps at One Spiked Level

Sample Name	Trap Solution Volume, mL	Dilution Factor	mg/L Chloride	Mass Spiked, µg Chloride	Mass Read, µg Chloride	Spike Recovery, %
146959 S1 +TR+P1+P2	50.0274	5	1.46	340	365	107.3
146959 S2 +P3	52.0853	5	<0.1			
146961 S1 +TR+P1+P2	50.8700	5	1.43	340	364	106.9
146961 S2 +P3	50.8371	5	<0.1			
146962 S1 +TR+P1+P2	52.2369	5	1.42	340	370	109.0
146962 S2 +P3	51.7783	5	<0.1			
146971 S1 +TR+P1+P2	51.0563	5	1.42	340	364	106.9
146971 S2 +P3	50.3973	5	<0.1			
					Average	107.5

Metals

Spiking metals on sorbent traps in a manner that would reproduce an actual field sample was not considered practical; however, an evaluation of sorbent background concentrations was performed. Analyses were performed on four sets of field blank MEST-M traps; results are shown in Table 13. Traps were recovered in two stages; the front stage S1 and back stage S2 were analyzed separately. While care was taken on trap material selection and fabrication, the

Table 12. Second Set of Spiked MEST-H Traps at Varying Spiked Levels Used During Field Sampling

Sample No.	Spike, µg	Read, µg	Recovery, %
1	350	371	106
2	350	383	109
3	700	751	107
4	700	736	105
5	1200	1257	105
6	1200	1262	105
		Average	106.2

Table 13. Analysis of MEST-M Field Blanks, µg/sample

	Sb	As	Be	Cd	Cr	Co	Pb	Mn	Hg	Ni	Se
U2-BLK1A S1	0.007	0.025	0.010	0.565	0.466	0.047	58.5	1.35	0.0005	1.35	0.05
U2-BLK2B S1	0.008	0.025	0.010	0.753	0.395	0.045	78.0	1.61	0.0008	2.26	0.05
U2-BLK3A S1	0.009	0.025	0.010	0.142	0.217	0.048	7.66	1.36	0.0010	2.16	0.05
U1-BLK4A S1	0.008	0.025	0.008	5.20	0.247	0.033	97.4	1.06	0.0005	2.32	0.05
Average	0.008	0.025	0.010	1.67	0.331	0.043	60.4	1.35	0.0007	2.02	0.05
U2-BLK1A S2	0.005	0.025	0.007	0.040	0.372	0.078	2.60	3.36	0.0005	0.451	0.05
U2-BLK2B S2	0.005	0.025	0.005	0.045	0.320	0.026	1.75	1.04	0.0009	0.820	0.05
U2-BLK3A S2	0.005	0.025	0.005	0.078	0.292	0.052	4.26	1.68	0.0011	0.662	0.05
U1-BLK4A S2	0.005	0.025	0.005	0.021	0.376	0.025	0.866	1.15	0.0008	1.54	0.05
Average	0.005	0.025	0.006	0.046	0.340	0.045	2.37	1.81	0.0008	0.868	0.05

data indicate a high degree of variability and significant bias for Pb between S1 and S2, suggesting a possible source of Pb (and possibly Cd) contamination during assembly. This high degree of variability makes background corrections difficult, resulting in highly variable Pb and Cd emissions when using the MEST-M method.

For nonmercury metals analysis, the ICP–MS instrument was calibrated with a blank and a minimum of three standards, which were prepared from commercially available stock standards traceable to the National Institute of Standards and Technology (NIST). The blank and standard diluent were 1% v/v HNO_3 prepared from concentrated trace metal-grade acid and ASTM International Type I water. After calibration, an initial calibration verification (ICV) standard was run, which required a reading of 95%–105% of the actual value or the instrument was recalibrated. The ICV was prepared from a source separate from the calibration standards. Calibration standards and ICVs were prepared daily.

A minimum of one sample out of every ten or one sample from each batch was analyzed in triplicate to determine instrument precision. Acceptable precision limits are <10% RSD. All sample replicates for this project were within the acceptable limits. Analyte spikes of known concentrations were prepared for each sample matrix and analyzed at the same frequency to confirm analyte recovery from a particular matrix. The amount of analyte added was approximately equal to the amount found in the sample. The solution used for spiking was prepared from a stock separate from the calibration standards. Acceptable ranges for analyte

recovery are 85%–115% for samples reading above the MDL and 50%–150% for samples reading below the MDL. All matrix spikes for this project were within the acceptable limits.

A continuing calibration verification (CCV) standard, prepared at a concentration equivalent to the midpoint range of the calibration curve, was run every ten samples and at the end of every run to check the slope of the calibration curve. The CCV had to read 90%–110% of the true value or the instrument was recalibrated and the samples since the last acceptable CCV were reanalyzed.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be drawn from the field tests for halogens:

- The MEST-H method was used to obtain HCl emission data for two units burning Illinois coal with varying flue gas temperatures and conditions. Sampling at the two units presented relatively high and low HCl emission levels, challenging the MEST-H over a wide range. The measured HCl stack concentrations at Unit 1 were above 40 ppmvd (at 3% O_2) and below the MATS limits (~1.8 ppmvdv at 3% O_2) at Unit 2.

- A statistical analysis was used to compare the relative bias and precision of the two methods. Results of the comparison of MEST-H and EPA Method 26A at Units 1 and 2 indicated no significant bias. At both units, the HCl emission measurements for each run showed excellent agreement between EPA Method 26A and the MEST-H method, generally within 5%–10%.

- For both units, the paired MEST-H traps showed good agreement, generally all less than 20% RD, with much of the data showing less than 10% RD. Relative accuracy was within 5%.

- Sampling at Unit 2 was more challenging and produced results that were more variable. Unit 2 operates at a fairly low stack temperature of approximately 130°–140°F, and the flue gas was oversaturated with moisture, resulting in water droplet formation and scrubber mist carryover. At these temperatures, mist carryover from the scrubber is likely to stay in liquid form and not vaporize. Sampling at these conditions is extremely difficult, both for the MEST-H method and M26A.

- Redesign of trap and material selection has reduced background contributions of HCl from the sorbent material by a factor of over 10. Blank values are ~100 times lower than the MATS limit for new/reconstructed coal-fired units, assuming a 250-L sample volume.

- While comparative and validation efforts focused on measurement of HCl, measurement data suggest that the MEST-H method can also be used for measurement of HBr, with results being comparable to M26A. For Unit 1, an apparent bias of approximately 40%–50% was shown, which is believed to be due to bromine that is

collected on the M26A filter and not included in the analyses. This phenomenon has been observed when bromine comes in contact with ash on a filter.

Based on these data and conclusions from previous tests, The MEST-H method shows promise as an alternative to EPA Method 26 or 26A for measuring HCl at the limits for both existing and new/reconstructed coal-fired units.

The following conclusions can be drawn from the field tests for HAP metals:

- Concentrations measured for Sb, As, Be, and Co were relatively low, mostly below the MATS limit, and for Sb below the M29 detection limit. Detection limits were generally lower for the MEST-M method of generally a factor of 2 better than M29 resulting in concentrations that were approximately 50% of M29 detection values.

- As shown at other plants, Cd, Cr, Pb, Mn, and Ni were shown to be much more variable, making comparison between MEST-M and M29 difficult. Measured values between the two methods were generally within 100%, with many of the values being within 50%. While precautions were taken to minimize trap Pb and Cd contamination, background contributions were still significant to measured emissions. Cr and Ni showed improved comparative results compared to previously sampled plants, likely because of relatively high concentrations and longer sampling duration. Comparatively, Mn values improved significantly with respect to previous measurements, with measurement generally within 50%.

- Although much improvement has been made in the sorbent trap background, additional effort is still needed to reduce these metals further. It should be further noted that EPA Method 29 also showed much more variability for these same metals and also has issues with background concentrations when attempting to measure at levels at or below the MATS limits defined for new sources.

- Hg and Se showed comparable results for both MEST-M and M29 for both units, generally within 20%.

- Determination of compliance values using either M29 or the MEST-M method to MATS limits for Sb, As, Be, and Co will be difficult because the regulatory limits are at or very near the detection limits for these elements. For these metals, M29 data showed values near detection limits, with lower limits reported by MEST-M.

- Background levels for Cd, Pb, Cr, Mn, and Ni preclude reliable determination of compliance to MATS limits defined for new sources. Both M29 and the MEST-M method have background values as determined by field blanks that are highly variable and near concentrations required to meet MATS for new sources.

- A sampling duration of 4 hours did appear to improve detection of low-concentration metals. Achieving measurements to determine compliance with MATS for existing sources will be challenging and require 4-hour, or longer, sampling durations.

- New source MATS for nonmercury metals are extremely low, requiring that sampling times may need to be extended beyond 4 hours, both for M29 and the MEST methods.

Based on these conclusions, additional research is still needed to explore possible longer sampling durations and/or selection of lower-background materials before the MEST-M method can be considered as a potential alternative method to Method 29 to demonstrate compliance for all of the trace metals listed in MATS.

Based on the results of these two field tests, the following recommendations are made for future research:

- Work with EPA to gain formal acceptance of the MEST-H as an alternative method to M26 (and 26A).

- Continue to evaluate the effect of different plant configurations on the applicability of the MEST method. In particular, units burning subbituminous coal, units equipped with SNCR, SCR, dry scrubbers, and fabric filters are of interest.

- Continue to refine the sampling and analysis process to improve (lower) detection limits.

- Evaluate a synthetic sorbent trap material to obtain lower background contributions of metals, in particular Cd, Pb, Ni, Cr, and Mn. A synthetic material has been identified that shows background concentrations on the order of 10–100 times less than trap material used to date.

- Evaluate longer sampling durations (6–8+ hours) to improve the accuracy of both the MEST-M method and EPA Method 29. A longer sampling duration would provide a greater sample mass compared to the blank levels.

- Explore the possibility of using the MEST-H traps in a continuous monitoring approach for HCl.

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APPENDIX A

MERCURY AND AIR TOXICS STANDARDS

HCl STANDARDS

Table A-1. MATS Limits and Corresponding Flue Gas Concentrations for HCl Emissions from Coal-Fired Power Plants

MATS Sources	MATS Published Limits	Approx. Limits, ppmv dry at 3% O_2	Approx. Limits, µg/dNm^3 at 3% O_2
Existing Coal-Fired Units	2.0×10^{-3} lb/MMBTu 2.0×10^{-2} lb/MWh	~1.8[a]	~2800[a]
New or Reconstructed Coal-Fired Units	1.0×10^{-2} lb/MWh	~0.9[a]	~1400[a]
Cement Kilns (existing and new kilns)	3.0 ppmvb (30-day average)	3.0[b] (~3.9 at 3% O_2)	~4600[b]

[a] Calculated values based on a net heat rate of 10,300 Btu/kWh.
[b] Corrected to 7% O_2.

METAL STANDARDS

Table A-2. MATS Limits and Corresponding Flue Gas Concentrations for Metal Emissions for Coal-Fired Power Plant Units

	Existing Units			New or Reconstructed Units		
Metal	MATS Limits (1, 2)	Approx. Limits[a] ppbv dry at 3% O_2	Approx. Limits[a] µg/dNm^3 at 3% O_2	MATS Limits [1, 2]	Approx. Limits[a] ppbv dry at 3% O_2	Approx. Limits[a] µg/dNm^3 at 3% O_2
Total Non-Hg Metals	50 lb/TBtu 0.50 lb/GWh	–	66.96	0.06 lb/GWh	–	7.96
Antimony	0.80 lb/TBtu 0.0080 lb/GWh	0.221	1.12	0.008 lb/GWh	0.221	1.12
Arsenic	1.1 lb/TBtu 0.020 lb/GWh	0.952	2.96	0.003 lb/GWh	0.143	0.44
Beryllium	0.20 lb/TBtu 0.0020 lb/GWh	0.748	0.28	0.0006 lb/GWh	0.237	0.09
Cadmium	0.30 lb/TBtu 0.0030 lb/GWh	0.090	0.42	0.0004 lb/GWh	0.013	0.06
Chromium	2.8 lb/TBtu 0.030 lb/GWh	1.814	3.92	0.007 lb/GWh	0.480	1.04
Cobalt	0.80 lb/TBtu 0.0080 lb/GWh	0.457	1.12	0.002 lb/GWh	0.121	0.30
Lead	1.2 lb/TBtu 0.020 lb/GWh	0.344	2.96	0.02 lb/GWh	0.344	2.96
Manganese	4.0 lb/TBtu 0.050 lb/GWh	3.244	7.40	0.004 lb/GWh	0.260	0.59
Mercury (low-rank coal)[b]	4.0 lb/TBtu 0.040 lb/GWh	0.650	5.42	0.040 lb/GWh	0.650	5.42
Mercury (non-low-rank coal)[c]	1.2 lb/TBtu 0.013 lb/GWh	0.201	1.68	0.003 lb/GWh	0.053	0.44
Nickel	3.5 lb/TBtu 0.040 lb/GWh	2.310	5.92	0.040 lb/GWh	2.310	5.92
Selenium	5.0 lb/TBtu 0.060 lb/GWh	2.709	8.89	0.05 lb/GWh	2.257	7.40

[a] Calculated values based on a heat rate of 10,000 Btu/kWh.
[b] Low-rank coal is <8300 Btu/lb.
[c] Non-low-rank coal is >8300 Btu/lb.

REFERENCES

1. National Emission Standards for Hazardous Air Pollutants from Coal- and Oil-Fired Electric Utility Steam Generating Units and Standards of Performance for Fossil-Fuel-Fired Electric Utility, Industrial-Commercial-Institutional, and Small Industrial-Commercial-Institutional Steam Generating Units: Final Rule (Mercury and Air Toxics Standards [MATS]). 40 Code of Federal Regulations, Parts 60 and 63; *Fed Regist*. **2012**, *77* (32), 9304.

2. Reconsideration of Certain New Source Issues: National Emission Standards for Hazardous Air Pollutants from Coal- and Oil-Fired Electric Utility Steam Generating Units and Standards of Performance for Fossil-Fuel-Fired Electric Utility, Industrial-Commercial-Institutional, and Small Industrial-Commercial-Institutional Steam Generating Units: Final Rule (Mercury and Air Toxics Standards [MATS]). 40 Code of Federal Regulations, Parts 60 and 63; *Fed Regist*. **2012**, *78* (79), 24073.

APPENDIX B

SAMPLING METHODS AND PROCEDURES

SAMPLING METHODS AND PROCEDURES

EPA STANDARD SAMPLING METHODS

Halogens (EPA Method 26 or 26A)

The reference method for halogens is U.S. Environmental Protection Agency (EPA) Method 26 or 26A (1). Details of Method 26A can be found at www.epa.gov/ttn/emc/promgate/m-26a.pdf. Method 26 (nonisokinetic) and Method 26A (isokinetic) are wet-chemistry, impinger-based methods. Method 26A must be used at units with suspended water droplets (wet stacks). In addition to HCl, Method 26 and 26A can be used to measure HBr, HF, Cl_2, and Br_2 emissions. Although this method claims to speciate Cl_2 and HCl with the addition of alkaline impingers, research has shown that the speciation can be biased in the presence of elevated sulfur dioxide (2). This is likely the case for Br_2 as well. Figure B-1 displays a schematic of Method 26A.

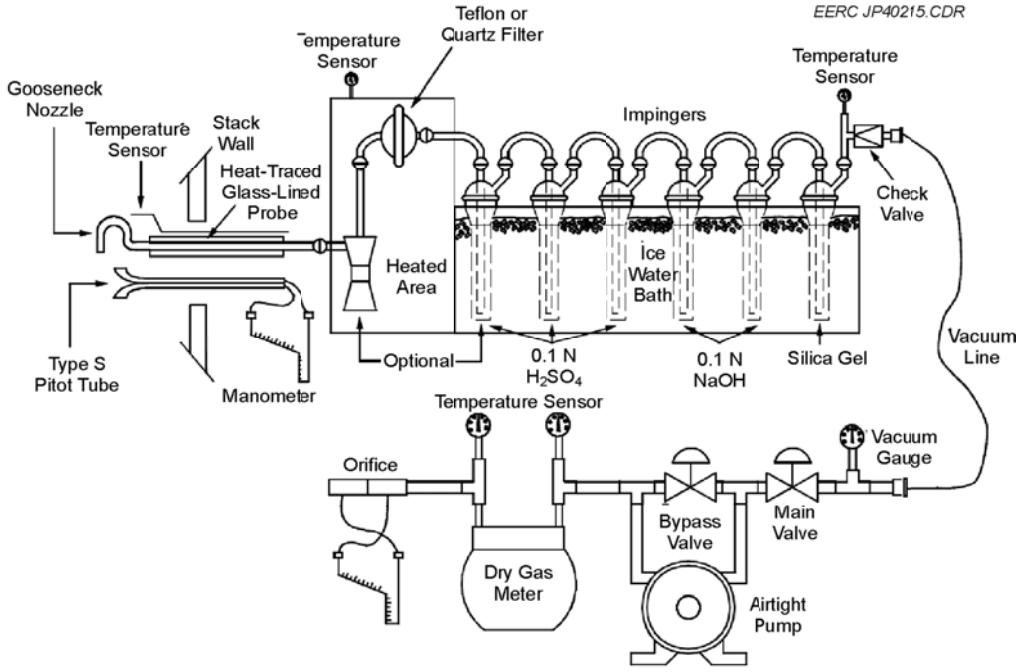

Figure B-1. Schematic of the EPA Method 26A sampling train.

The published method detection limits (MDLs) for HCl by Methods 26 and 26A are 0.01 and 0.04 ppmvd, respectively, assuming a 1-dry-standard-cubic-meter sample. These detection limits do not take into account the uncertainty and errors associated with sample collection and possible biases.

Methods 26 and 26A are known to be impacted by both positive and negative biases. A high bias for HCl may occur in the presence of chlorine dioxide and ammonium chloride (3). Method 26A states that HBr can cause a positive bias by converting molecular chlorine (if present) to HCl. There is also a potential for a low bias for HCl at concentrations under 20 ppmvd, caused by moisture in the flue gas (4). This bias can be reduced by operating the probe at higher temperatures in an attempt to ensure that no water droplets are collected on probe surfaces. However, there is still likely to be some associated error or bias. The low bias can be especially severe if samples are taken after a wet scrubber because of the potential for scavenging of the HCl by the entrained water droplets. The isokinetic sampling specified in EPA Method 26A helps to minimize this problem, but condensation in the probe can still result in a low bias if there are cold spots in the probe and sampling line before the impingers or if the heat input is insufficient to evaporate the water droplets before they contact the probe surfaces. Low-level halogen measurements taken after a wet scrubber or at high moisture levels, are likely to be biased low, and this would also be true when using the optional cyclone at the probe inlet.

EPA reported in "Stack Sampling Methods for Halogens and Halogen Acids" (4), that the low bias in EPA Method 26A was not consistent from test to test but could be roughly correlated with the moisture content of the flue gas. Tests at 4.8 ppmv HCl indicated a low bias of 50%. Another test indicated that spiked impinger recoveries were reasonable but that recovery of spikes introduced at the probe tip were low by a factor of 3 to 5 (4). The presence of ammonium chloride (NH_4Cl) was found to produce a positive bias in all cases, and any attempt to mitigate this bias by adjusting temperature aggravated the moisture bias. In flue gases containing ammonia slip, it could be assumed that the high bias for HCl due to NH_4Cl could be as high as the ammonia slip value in the flue gas if the ammonia reacted with available Cl^- ions. If ammonia emissions are over 10 ppmv, the potential high bias for HCl using EPA Method 26A could be several times the MATS limit for existing plants and could be as high as 10 ppmv. This 10-ppmv bias would make it impossible to demonstrate emission compliance for utilities. Even at a more typical ammonia slip of <5 ppm, there is potential for significant impact.

Analysis of samples by EPA Method 26A is typically done using ion chromatography (IC). IC is the preferred analysis method because of its ability to analyze for all of the halogens and its suitability for automated systems, which greatly increase sample throughput. The IC instrument/laboratory detection limit of 0.1 mg/L for halogens is significantly lower than required for the MATS emission limits, assuming a minimum sampling duration of 2 hours. This shows that the analytical instrumentation is capable of providing adequate detection levels to measure HCl at the levels required by MATS for existing plants but may not be able to measure accurately at the extremely low limits for new/reconstructed coal and oil-fired units.

Mercury and Nonmercury Metal HAPs (EPA Method 29)

The reference method for mercury and nonmercury metal HAPs is EPA Method 29 (5) available at www.epa.gov/ttn/emc/promgate/m-29.pdf. The method was designed to measure the solid particulate and gaseous emissions of mercury and 16 other trace elements. A schematic of the EPA Method 29 sampling train is presented in Figure B-2. The EPA Method 29 sampling train consists of a particulate filter and seven impingers.

The filter is used to collect particulate-phase metals. Following an optional moisture knockout impinger, gaseous species are collected in two pairs of impingers connected in series containing different absorption solutions. The non-Hg gaseous metals, along with oxidized vapor-phase Hg, are captured in the first pair of impingers containing aqueous solutions of 5% nitric acid (HNO_3) and 10% hydrogen peroxide (H_2O_2), while the elemental Hg is captured in a second pair of impingers containing aqueous solutions of 4% potassium permanganate ($KMnO_4$) and 10% sulfuric acid (H_2SO_4). An empty impinger is located between the two sets of impingers to reduce the potential for blowback of $KMnO_4$ into the second HNO_3/H_2O_2 impinger during leak checks. The last impinger in the sampling train contains silica gel to prevent contamination and entrap moisture that may otherwise travel downstream and damage the dry gas meter and pump. Stack testers may omit the permanganate impingers and measure mercury separately with a sorbent trap method such as Method 30B.

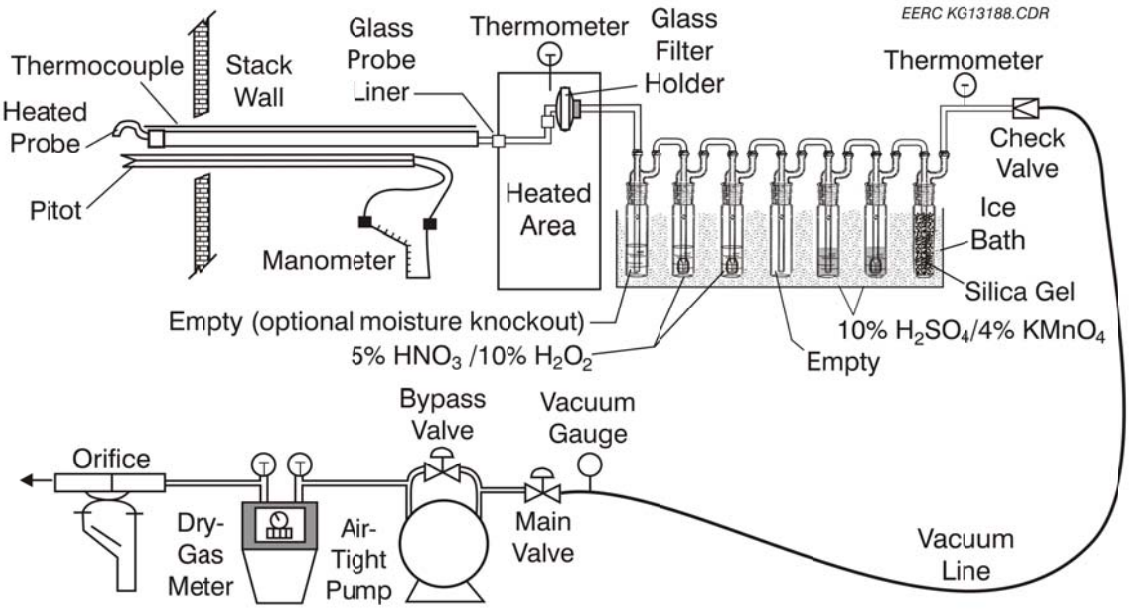

Figure B-2. Schematic of the EPA Method 29 sampling train.

The published detection limits for EPA Method 29 for a sample volume of 1.25 m^3 are shown in Table B-1. These values were calculated from instrument detection limits for primarily graphite furnace atomic absorption spectroscopy (GFAAS), with the exception of Ni which was determined from the detection limit of inductively coupled plasma–atomic emission spectroscopy (ICP–AES) and Hg via cold-vapor atomic absorption spectroscopy (CVAAS). Also in Table B-1, the detection limits using inductively coupled plasma–mass spectroscopy (ICP–MS) are presented (sample volume of 1.0 m^3). As shown, much lower concentrations can be obtained using ICP–MS. However, to measure these values, blank levels must be kept very low and the impingers contaminant-free. With very careful sampling and analysis, these detection limits can be obtained, but practical detection limits are often 50% to 100% higher because of added sources of uncertainty sampling procedures, especially when conducting field sampling. Detection limits can be improved by increasing the sampling time; however, other flue gas constituents may consume the impinger chemicals, causing the values to be biased low. It should be noted that the detection limits for mercury have improved by a factor of 10 as a result of improvement in analysis technology since EPA Method 29 was published in 2000.

MEST Sorbent Trap Sampling Methods

The EERC has developed two novel sorbent trap-based methods that can be used to sample for trace elements and/or halogens (with a focus on HCl). Although the proprietary sorbent trap materials differ, the sampling procedures and equipment used to capture HCl and trace metals are very similar. The sample traps are illustratively shown in Figure B-3 and pictorially in Figure B-4, in an isokinetic configuration. Both isokinetic and non-isokinetic traps were used in this project.

Table B-1. Detection Limits of EPA Method 29

	Published EPA Method 29 Detection Limits with GFAAS, µg/dNm^3	EPA Method 29 Detection Limits with ICP–MS, µg/dNm^3
Antimony	1.1	0.1
Arsenic	0.4	0.5
Beryllium	0.08	0.1
Cadmium	0.03	0.1
Chromium	0.3	0.1
Cobalt	0.3	0.5
Lead	0.3	0.1
Manganese	0.3	0.1
Mercury	0.56	0.01
Nickel	5.4	0.2
Selenium	0.8	1

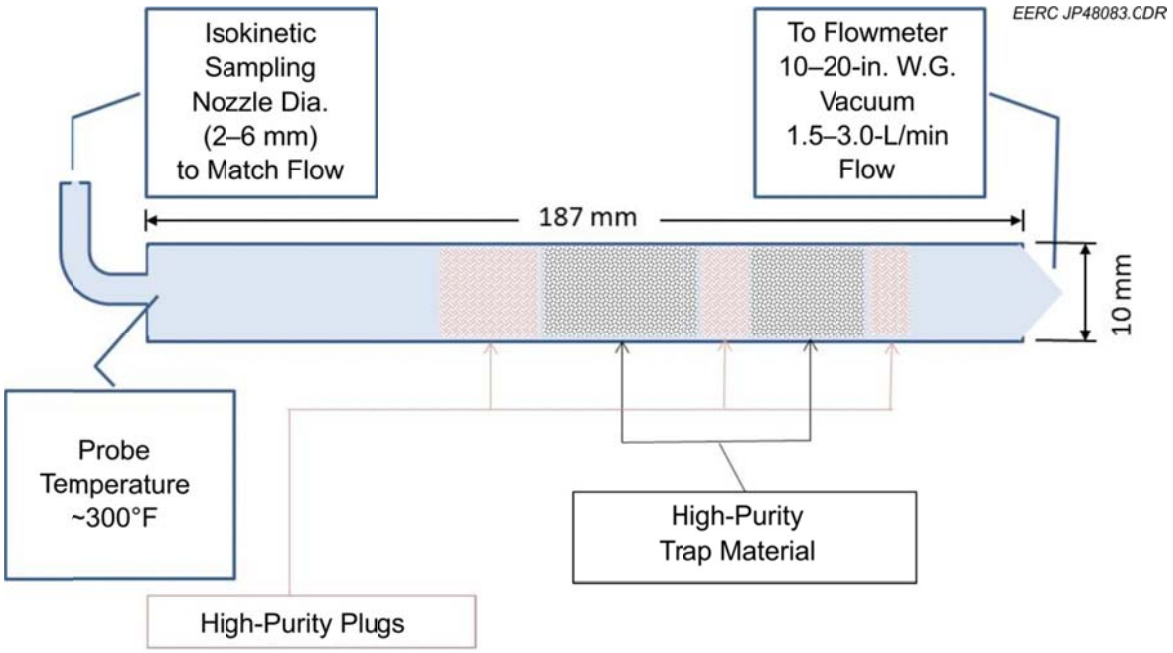

Figure B-3. Conceptual view of MEST.

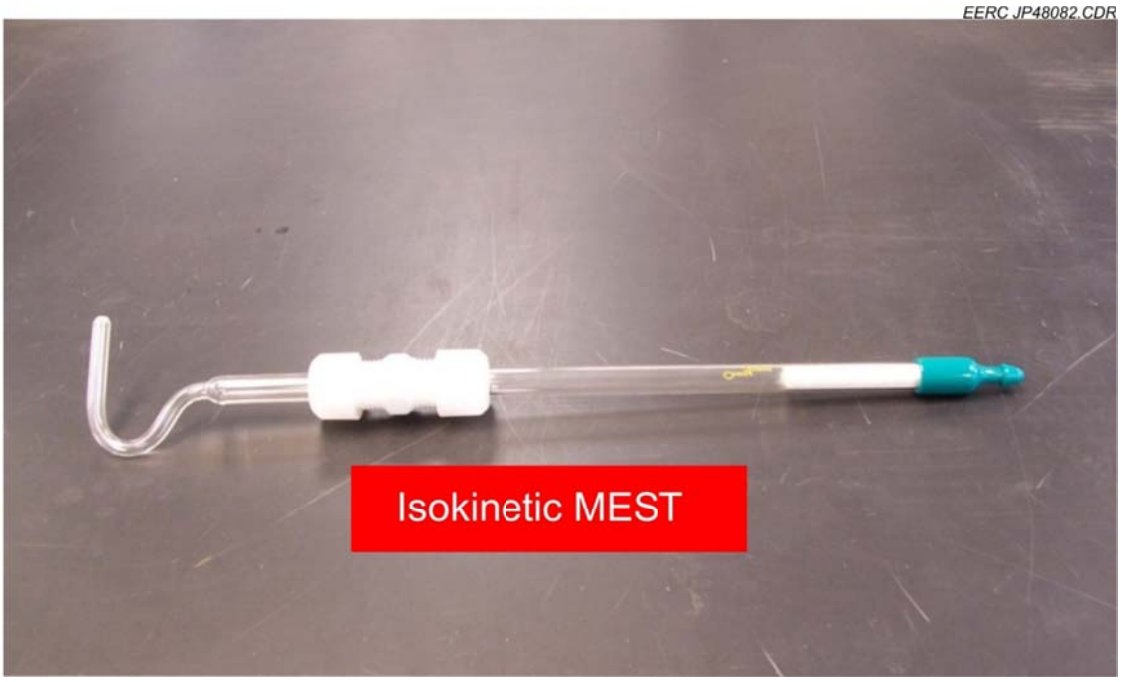

Figure B-4. Example photo of MEST.

Both the MEST-M and MEST-H methods draw an isokinetic flue gas sample through a series of plugs and trap materials, as shown in Figure B-3 (it should be noted that MEST-H can also be used for nonisokinetic sampling). The metals and/or halogens are targeted for capture in the first plug-and-trap section. The second trap serves as a quality check to make sure that none of the metals and/or halogens (HCl) break through the first trap. The sampling procedures are similar to those used in EPA Method 30B: "Determination of Total Vapor-Phase Mercury Emissions from Coal-Fired Combustion Sources Using Carbon Sorbent Traps" (www.epa.gov/ttn/emc/promgate/Meth30B.pdf).

MEST-H Method for Halogens

The MEST-H method was designed for isokinetic sampling, which is required for flue gas with high-relative-moisture content (EPA Method 26A), but it also can be used for nonisokinetic sampling in dry flue gas environments (EPA Method 26). Approximately 250 L of flue gas is drawn through a series of glass wool plugs and beds of proprietary sorbent material (shown in Figure B-3). The glass wool plug is intended to capture particulate matter that may enter the trap, similar to the filter of EPA Method 26/26A. The glass wool plug is also analyzed for HCl. The trap material is formulated to capture halogen compounds, in particular, HCl. To ensure that condensation does not form, the MEST-H trap is maintained at the sampling flue gas temperature or 300°F, whichever is higher.

MEST-M Method for Trace Metals

Similar to the MEST-H method, the MEST-M method draws an isokinetic flue gas sample of approximately 250 L through a series of quartz plugs and beds of proprietary sorbent. However, the trap material that is used is formulated to target capture of the trace elements regulated by MATS. To ensure that condensation does not form, the MEST-M trap is maintained at the sampling flue gas temperature or 300°F, whichever is higher.

REFERENCES

1. U.S. Environmental Protection Agency. Method 26A – Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources—Isokinetic Method. 40 Code of Federal Regulations, Part 60, Appendix A-8, Method 26A (issued March 3, 1994).

2. Sun, J.Q.; Crocker, C.R.; Lillemoen, C.M. The Effect of Coal Combustion Flue Gas Components on Low-Level Chlorine Speciation Using EPA Method 26A. *J. Air Waste Manage. Assoc.* **2000**, *50* (6), 936–40.

3. Johnson, L.D. Stack Sampling Methods for Halogens and Halogen Acids. Presented at the EPA/AWMA International Symposium on Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, May 1996.

4. 4B Field Evaluation of a Novel Sorbent Trap Method for Measuring Metal and Halogen Emissions. EPRI, Palo Alto, CA: 2013. 3002001065.

5. *Standard Methods for the Examination of Water and Wastewater*, 19th Edition; 1995, 1030 E. Method Detection Level, p 1–10.

6. U.S. Environmental Protection Agency. Method 29 – Determination of Metals Emissions from Stationary Sources. 40 Code of Federal Regulations, Part 60, Appendix A-8, Method 29 (www.epa.gov/ttn/emc/promgate/m-29.pdf) (issued June 25, 1996).

APPENDIX C

TRACE METAL RESULTS

Table C-1. Unit 1 Flue Gas Metal Concentrations: U.S. Environmental Protection Agency Method 29, µg/dNm^3 at 3% O_2

		Sb	As	Be	Cd	Cr	Co	Pb	Mn	Hg	Ni	Se
Unit 1 M29-1	µg/dNm^3	<0.2	1.94	0.614	0.586	8.77	2.13	11.4	20.7	0.0730	6.00	1.31
Unit 1 M29-2	µg/dNm^3	<0.2	1.82	0.677	0.436	7.34	1.95	9.37	17.8	0.0451	4.66	1.11
Unit 1 M29-3	µg/dNm^3	<0.2	1.68	0.669	0.536	7.57	2.09	10.1	21.9	0.0605	4.80	1.21
Unit 1 M29-4	µg/dNm^3	<0.2	1.61	0.653	0.481	7.39	1.98	11.0	21.4	0.0692[a]	4.38	1.08
Average	µg/dNm^3	<0.2	1.76	0.653	0.510	7.77	2.04	10.5	20.5	0.0620	4.96	1.18
Standard	µg/dNm^3		0.13	0.024	0.057	0.58	0.08	0.8	1.6	0.012	0.62	0.09
RSD[e]	%		7	4	11	8	4	7	8	20	12	8

[a] Blank-corrected (blank >10% of sample value).
[b] Blank-corrected (blank >30% of sample value).
[c] Blank-corrected to below detection limit.
[d] Relative difference (RD) for duplicate traps >20%.
[e] Relative standard deviation (RSD).

Table C-2. Unit 1 Determination of the Relative Difference (RD) for the MEST-M (multielement sorbent trap-M) Samples, µg/dNm^3 at 3% O_2

	Trap	Sb	As	Be	Cd	Cr	Co	Pb	Mn	Hg	Ni	Se
TM-1	A	0.078[a]	0.934	0.230	0.026[c]	10.4	1.24	0.419	32.2	0.0482	10.9[a]	1.26
TM-1	B	0.074[a]	0.693	0.207	0.013[c]	9.52	1.12	0.395	29.2	0.0449	10.7[a]	0.444
RD, %		2.7	14.8	5.1	31.5[d]	4.5	5.0	3.0	4.9	3.6	1.0	47.8[d]
TM-2	A	0.066[a]	0.834	0.252	14.1[a]	8.81	1.15	190[b]	23.5[a]	0.0453	7.00[b]	1.12
TM-2	B	0.045[a]	0.537	0.276	0.055[c]	6.99	0.699[a]	1.31	15.9[a]	0.0321	3.74[b]	0.357
RD, %		18.5	21.6[d]	4.5	99.2[d]	11.5	24.2[d]	98.6[d]	19.4	17.1	30.4[d]	51.8[d]
TM-3	A	0.064[a]	0.557	0.161[a]	8.87[a]	9.96	0.995	287[a]	32.2	0.0533	5.24[b]	1.18
TM-3	B	0.058[a]	0.490	0.171[a]	15.6[a]	9.91	1.04	539[a]	27.9	0.0452	4.39[b]	1.08
RD, %		5.0	6.4	3.0	27.4[d]	0.3	2.0	30.6[d]	7.0	8.2	8.8	4.7
TM-4	A	0.055[a]	0.504	0.238	7.07	11.4[a]	0.925	94.8[b]	33.2	0.0375	5.71[b]	0.474
TM-4	B	0.062[a]	0.548	0.200	1.68[b]	9.87	0.882	102[b]	28.2	0.0451	2.67[b]	0.510
RD, %		6.2	4.1	8.8	61.7[d]	7.3	2.4	3.6	8.1	9.2	36.2[d]	3.7

[a] Blank-corrected (blank >10% of sample value).
[b] Blank-corrected (blank >30% of sample value).
[c] Blank-corrected to below detection limit.
[d] Relative difference (RD) for duplicate traps >20%.
[e] Relative standard deviation (RSD).

Table C-3. Unit 1 Flue Gas Metal Concentrations: MEST-M (multielement sorbent trap-metal), µg/dNm^3 at 3% O_2

		Sb	As	Be	Cd	Cr	Co	Pb	Mn	Hg	Ni	Se
Unit 1 TM-1	µg/dNm^3	0.076[a]	0.814	0.218	0.019[c,d]	10.0	1.18	0.407	30.7	0.0466	10.8[a]	0.850[d]
Unit 1 TM-2	µg/dNm^3	0.056[a]	0.686[d]	0.264	7.1[c,d]	7.90	0.922[a,d]	95.9[b,d]	19.7[a]	0.0387	5.37[b]	0.739[d]
Unit 1 TM-3	µg/dNm^3	0.061[a]	0.524	0.166[a]	12.2[a,d]	9.93	1.02	413[a,d]	30.1	0.0492	4.82[b]	1.13
Unit 1 TM-4	µg/dNm^3	0.059[a]	0.526	0.219	4.37[b,d]	10.7[a]	0.904	98.3[b]	30.7	0.0413	4.19[b,d]	0.492
Average	µg/dNm^3	0.063[a]	0.637	0.217	5.9[c,d]	9.61	1.01	152[b,d]	27.8	0.0439	6.29[b]	0.803[d]
Standard	µg/dNm^3	0.009	0.140	0.040	5.1	1.20	0.13	180	5.4	0.005	3.03	0.265
RSD[e]	%	15	22	18	86	12	13	118	19	11	48	33

[a] Blank-corrected (blank >10% of sample value).
[b] Blank-corrected (blank >30% of sample value).
[c] Blank-corrected to below detection limit.
[d] Relative difference (RD) for duplicate traps >20%.
[e] Relative standard deviation (RSD).

Table C-4. Unit 2 Flue Gas Metal Concentrations: U.S. Environmental Protection Agency Method 29, µg/dNm^3 at 3% O_2

		Sb	As	Be	Cd	Cr	Co	Pb	Mn	Hg	Ni	Se
Unit 2 M29-1	µg/dNm^3	<0.3	4.60	0.144	0.242	57.8	0.784	5.04	19.5	0.799	35.3	35.6
Unit 2 M29-2	µg/dNm^3	0.31	4.26	0.044	0.133	63.7	0.609	4.41	23.8	0.698	24.7	46.5
Unit 2 M29-3	µg/dNm^3	<0.3	4.21	0.053	0.308	88.2	0.757	6.14[a]	26.1	0.856	42[b]	35.8
Unit 2 M29-4	µg/dNm^3	<0.3	4.50	0.047	0.150	74.4	0.802	4.42	27.2	0.951	41.2	28.6
Unit 2 M29-5	µg/dNm^3	<0.3	4.56	0.063	0.274	52.2	0.638	5.64	34.7[a]	0.773	27.1	41.0
Unit 2 M29-6	µg/dNm^3	<0.3	4.56	0.057	0.194	107	0.951	4.55	25.7	1.40	55.4	39.6
Unit 2 M29-7	µg/dNm^3	<0.3	3.87	0.074	0.242	52.1	0.823	6.17	23.0	0.683	29.9	42.0
Unit 2 M29-8	µg/dNm^3	<0.3	4.43	0.146	0.241	37.0	0.661	7.30	24.5	1.15	22.6	42.8
Unit 2 M29-9	µg/dNm^3	<0.3	3.55	0.072	0.289	22.1	0.428	5.27	15.0	1.21	14.3	65.0
Unit 2 M29-10	µg/dNm^3	<0.3	3.32	0.070	0.217	40.1	0.504	5.45	21.3	1.08	26.8	47.9
Average	µg/dNm^3	<0.3	4.19	0.077	0.229	59.4	0.696	5.44	24.1	0.960	31.9	42.5
Standard	µg/dNm^3		0.46	0.037	0.057	25.1	0.158	0.92	5.2	0.241	11.8	9.7
RSD[e]	%		11	48	25	42	23	17	21	25	37	23

[a] Blank-corrected (blank >10% of sample value).
[b] Blank-corrected (blank >30% of sample value).
[c] Blank-corrected to below detection limit.
[d] Relative difference (RD) for duplicate traps >20%.
[e] Relative standard deviation (RSD).

Table C-5. Unit 2 Determination of the Relative Difference (RD) for the MEST-M Samples, µg/dNm^3 at 3% O_2

	Trap	Sb	As	Be	Cd	Cr	Co	Pb	Mn	Hg	Ni	Se
TM-1	A	0.023[c]	1.87	0.037[b]	0.029	8.48[a]	0.21[b]	0.42	36.1[a]	0.787	5.76[b]	36.0
TM-1	B	0.033[b]	2.78	0.069	0.089[c]	7.24[b]	2.41[b]	62.8[b]	201[a]	0.868	4.39[b]	49.1
RD, %		19.4	19.5	29.6[d]	50.4[d]	7.9	83.9[d]	98.7[d]	69.6[d]	4.9	13.5	15.4
TM-2	A	0.033[b]	2.52	0.059[b]	1.61	12.5	0.849[b]	48.5[b]	117[a]	0.732	1070	50.0
TM-2	B	0.032[b]	2.4	0.061[b]	0.275[b]	8.34[b]	0.15[b]	16.1[a]	31.3[b]	0.834	4.29[b]	52.1
RD, %		0.7	3.3	1.8	70.7[d]	19.9	70.1[d]	50.2[d]	57.7[d]	6.5	99.2[d]	2.1
TM-3	A	0.083[b]	2.25	0.074[a]	<0.01[c]	2.66[a]	0.387[a]	0.296	16.6	0.869	467[a]	50.3
TM-3	B	0.076[b]	2.06	0.060[b]	<0.01[c]	4.71[b]	0.113[b]	0.669	20.7[b]	0.865	0.285	51.4
RD, %		4.4	4.4	10.7	0.1	27.8[d]	54.8[d]	38.7[d]	11.0	0.2	99.9[d]	1.1
TM-4	A	0.151[a]	2.51	0.054[b]	0.036[c]	19.4	0.40[b]	0.657	123	1.03	217	54.9
TM-4	B	0.124[b]	2.14	0.056[b]	0.080[c]	14.5[b]	0.24[b]	7.61[b]	37.3[a]	1.01	20.5[a]	49.9
RD, %		9.7	7.8	1.8	37.7[d]	14.5	25.6[d]	84.1[d]	53.3[d]	1.0	82.7[d]	4.8
TM-5	A	0.094[b]	3.07	0.077[b]	0.15[c]	12.2[a]	0.21[b]	10.0[b]	26.5[b]	0.918	6.66[b]	52.8
TM-5	B	0.059[c]	2.98	0.056[b]	2.39[b]	12.8[a]	0.45[a]	149[b]	22.0[b]	0.839	4.36[b]	40.1
RD, %		22.8[d]	1.4	16.2	88.2[d]	2.5	35.1[d]	87.4[d]	9.4	4.5	20.8[d]	13.6
TM-6	A	0.040[b]	2.23	0.048[b]	1.62	8.86[b]	0.48[a]	115	33.8[a]	1.55	25.1[a]	43.0

[a] Blank-corrected (blank >10% of sample value).
[b] Blank-corrected (blank >30% of sample value).
[c] Blank-corrected to below detection limit.
[d] Relative difference (RD) for duplicate traps >20%.
[e] Relative standard deviation (RSD).

Continued...

Table C-5. Unit 2 Determination of the Relative Difference (RD) for the MEST-M Samples, µg/dNm^3 at 3% O_2 (continued)

	Trap	Sb	As	Be	Cd	Cr	Co	Pb	Mn	Hg	Ni	Se
TM-6	B	0.030[b]	2.28	0.034[b]	0.411[a]	11.5[b]	0.16[c]	12.3[b]	22.3[b]	1.58	9.97[b]	34.5
RD, %		14.4	1.2	17.3	59.6[d]	13.1	49.8[d]	80.6[d]	20.6[d]	1.1	43.2[d]	11.0
TM-7	A	0.078[c]	2.68	0.063[b]	0.11[c]	20.3[a]	0.318[b]	2.2[c]	34.4[b]	0.917	3.85[b]	45.7
TM-7	B	0.053[c]	2.30	0.053[b]	<0.01[c]	13.5[a]	0.15[c]	0.499	18.5[b]	0.783	2.19	47.1
RD, %		19.0	7.6	8.6	78.5[d]	20.1[d]	35.9[d]	63.7[d]	30.1[d]	7.9	27.4[d]	1.5
TM-8	A	0.055[c]	1.92	0.044[b]	0.278[b]	5.94[b]	0.195[b]	14.7[b]	30.7[b]	1.19	1.41[b]	43.0
TM-8	B	0.055[a]	2.26	0.064[b]	0.075[b]	12.4[a]	0.19[c]	0.689	19.3[b]	1.20	3.04[b]	49.6
RD, %		0.5	8.2	17.8	57.6[d]	35.2[d]	1.1	91.1[d]	22.8[d]	0.4	36.5[d]	7.1
TM-9	A	0.037[b]	1.52	0.038[b]	0.24[c]	2.70[a]	0.12[c]	23.9[b]	2.14	1.12	2.37[b]	45.6
TM-9	B	0.422	0.745	<0.01[c]	2.34	1534	12.7	109	86.7[a]	1.04	1159	32.8
RD, %		83.8[d]	34.3[d]	46.3[d]	81.5[d]	99.6[d]	98.2[d]	64.0[d]	95.2[d]	3.3	99.6[d]	16.3
TM-10	A	0.045[b]	1.46	0.053[b]	2.12[b]	8.27[b]	0.307[b]	182[b]	29.7[a]	1.22	1.10[b]	42.8
TM-10	B	0.047[b]	1.57	0.048[b]	1.17[b]	3.41[a]	0.127[b]	132[b]	13.9[b]	1.12	2.05[b]	47.9
RD, %		2.2	3.6	5.4	29.0[d]	41.6[d]	41.5[d]	16.0	36.2[d]	4.4	30.1[d]	5.6

[a] Blank-corrected (blank >10% of sample value).
[b] Blank-corrected (blank >30% of sample value).
[c] Blank-corrected to below detection limit.
[d] Relative difference (RD) for duplicate traps >20%.
[e] Relative standard deviation (RSD).

Table C-6. Unit 2 Flue Gas Metal Concentrations: MEST-M (multielement sorbent trap-M), µg/dNm^3 at 3% O_2

		Sb	As	Be	Cd	Cr	Co	Pb	Mn	Hg	Ni	Se
Unit 2 TM-1	ug/dNm^3	0.028[c,d]	2.32	0.053[b,d]	0.059[c,d]	7.86[b]	1.31[b,d]	31.6[b,d]	119[a,d]	0.827	5.08[b]	42.5
Unit 2 TM-2	ug/dNm^3	0.032[b]	2.44	0.060[b]	0.941[b,d]	10.4[b,d]	0.499[b,d]	32.3[b,d]	74.0[b,d]	0.783	537[b,d]	51.1
Unit 2 TM-3	ug/dNm^3	0.080[b]	2.16	0.067[b]	0.013[c,d]	3.69[b,d]	0.250[b,d]	0.482[d]	18.7[b]	0.867	234[a,d]	50.9
Unit 2 TM-4	ug/dNm^3	0.138[b]	2.33	0.055[b]	0.058[c]	16.9[b]	0.317[b,d]	4.13[b,d]	80.0[a,d]	1.02	119[a,d]	52.4
Unit 2 TM-5	ug/dNm^3	0.077[c]	3.02	0.066[b]	1.3[c,d]	12.5[a]	0.331[b,d]	79.4[b,d]	24.2[b]	0.878	5.51[b,d]	46.4
Unit 2 TM-6	ug/dNm^3	0.035[b]	2.26	0.041[b]	1.02[a,d]	10.2[b]	0.32[c,d]	63.5[b,d]	28.0[b,d]	1.57	17.6[b,d]	38.8
Unit 2 TM-7	ug/dNm^3	0.065[c]	2.49	0.058[b]	0.062[c,d]	16.9[a,d]	0.23[c,d]	1.4[c,d]	26.5[b,d]	0.850	3.02[b,d]	46.4
Unit 2 TM-8	ug/dNm^3	0.055[c]	2.09	0.054[b]	0.176[b,d]	9.18[b,d]	0.19[c]	7.71[b,d]	25.0[b,d]	1.20	2.22[b,d]	46.3
Unit 2 TM-9	ug/dNm^3	0.229[b,d]	1.13[d]	0.026[c]	1.3[c,d]	768[a,d]	6.4[c,d]	66.5[b,d]	44.4[a,d]	1.08	581[b,d]	39.2
Unit 2 TM-10	ug/dNm^3	0.046[b]	1.52	0.050[b]	1.64[b,d]	5.84[b,d]	0.217[b,d]	157[b]	21.8[b,d]	1.17	1.57[b,d]	45.4
Average	ug/dNm^3	0.078[c]	2.18	0.053[b]	0.65[c,d]	10.4[b,d]	1.0[c,d]	44.4[b,d]	46.1[b,d]	1.02	151[b,d]	45.9
Standard	ug/dNm^3	0.062	0.52	0.012	0.64	4.53	1.9	49.3	33.6	0.24	228	4.7
RSD	%	79	24	23	98	44	191	111	73	23	152	10

[a] Blank-corrected (blank >10% of sample value).
[b] Blank-corrected (blank >30% of sample value).
[c] Blank-corrected to below detection limit.
[d] Relative difference (RD) for duplicate traps >20%.
[e] Relative standard deviation (RSD).

APPENDIX D

METALS METHODS COMPARATIVE RESULTS

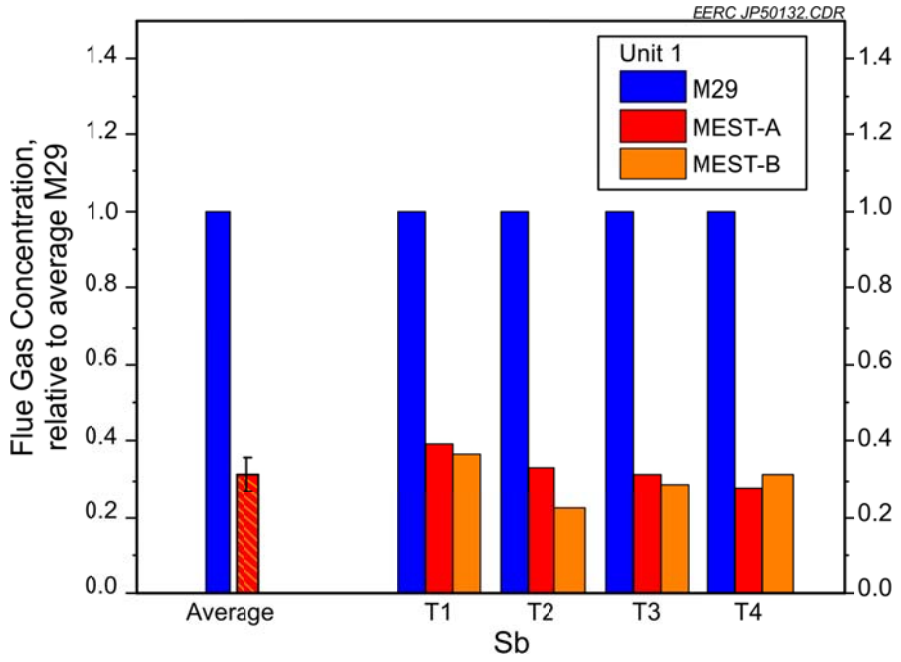

Figure D-1. Comparison of Sb between MEST-M and M29 (Unit 1).

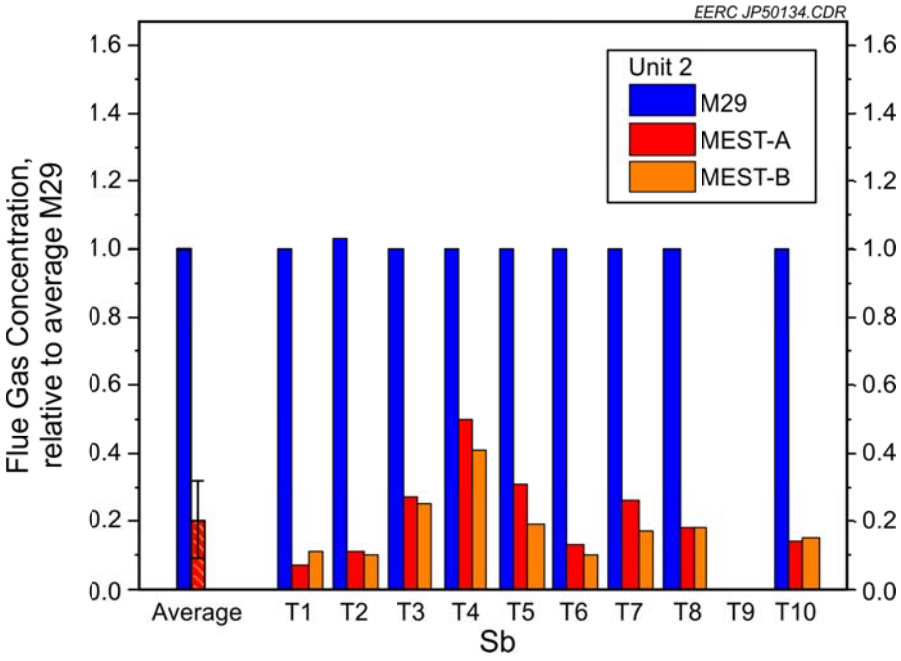

Figure D-2. Comparison of Sb between MEST-M and M29 (Unit 2).

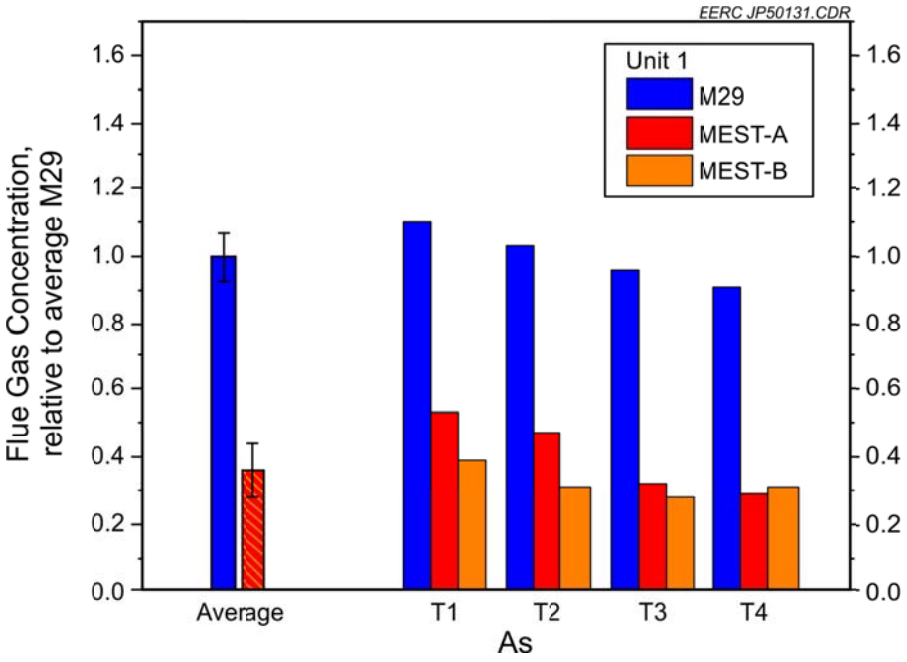

Figure D-3. Comparison of As between MEST-M and M29 (Unit 1).

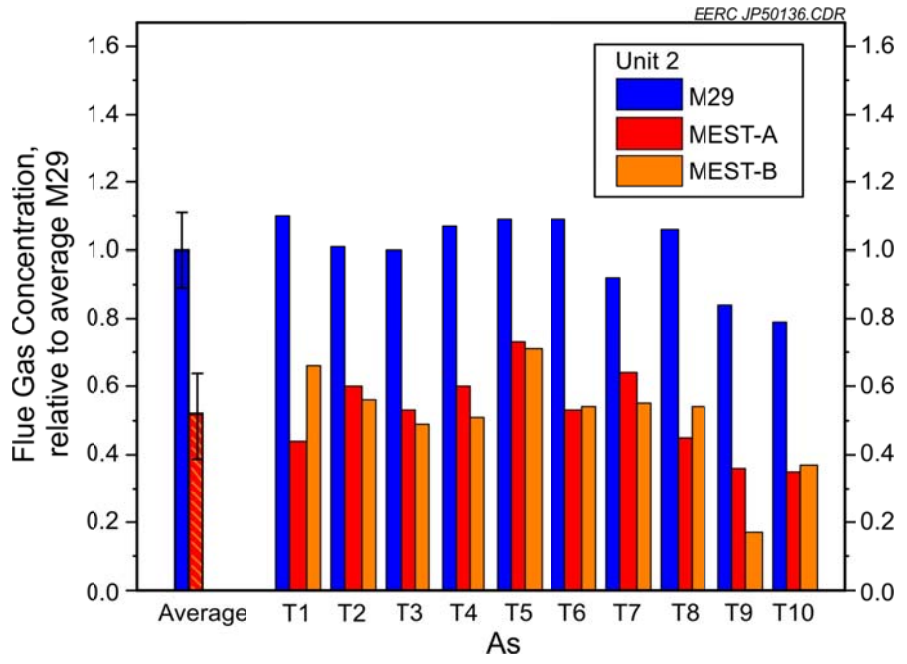

Figure D-4. Comparison of As between MEST-M and M29 (Unit 2).

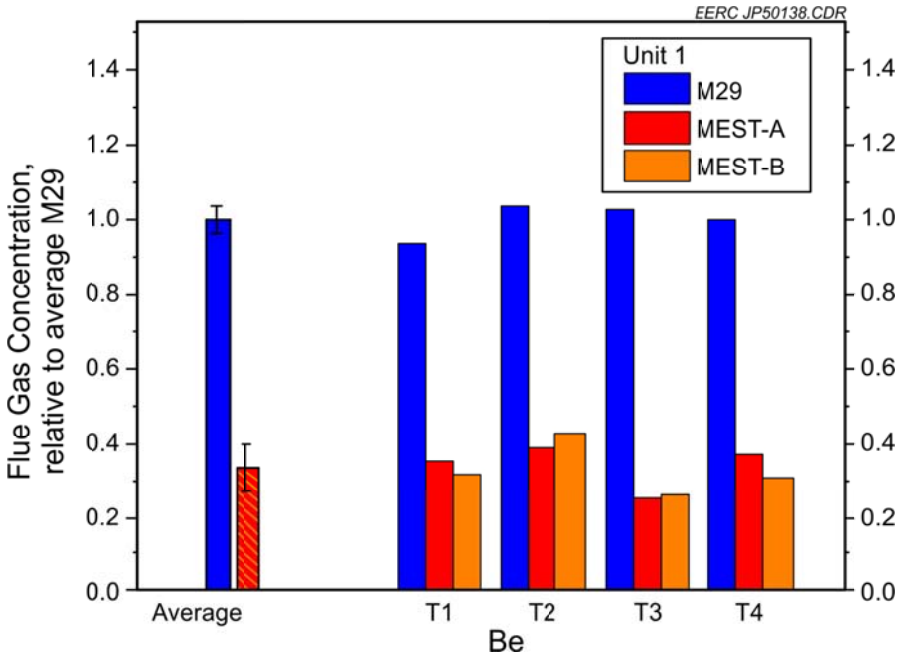

Figure D-5. Comparison of Be between MEST-M and M29 (Unit 1).

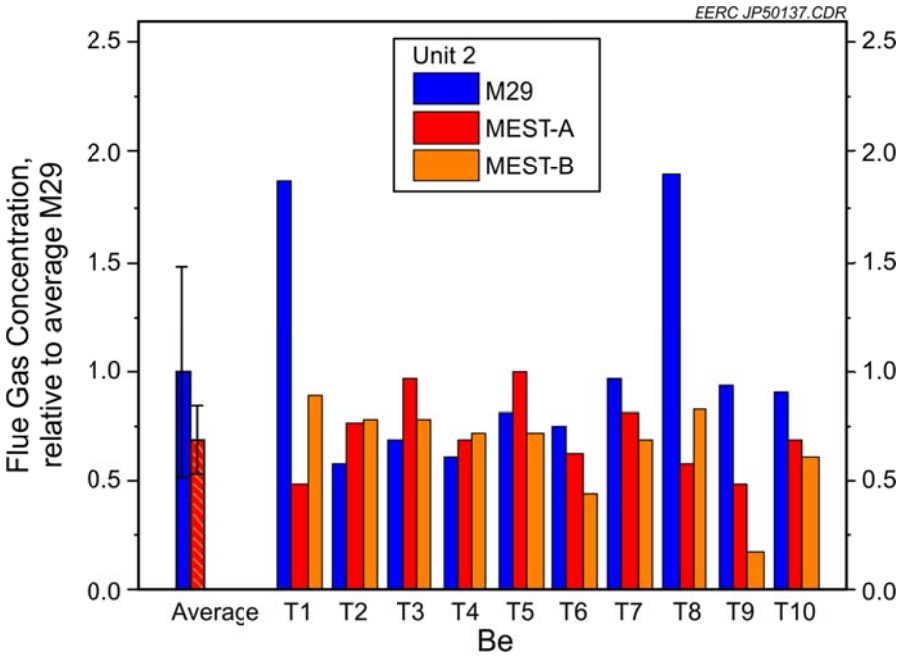

Figure D-6. Comparison of Be between MEST-M and M29 (Unit 2).

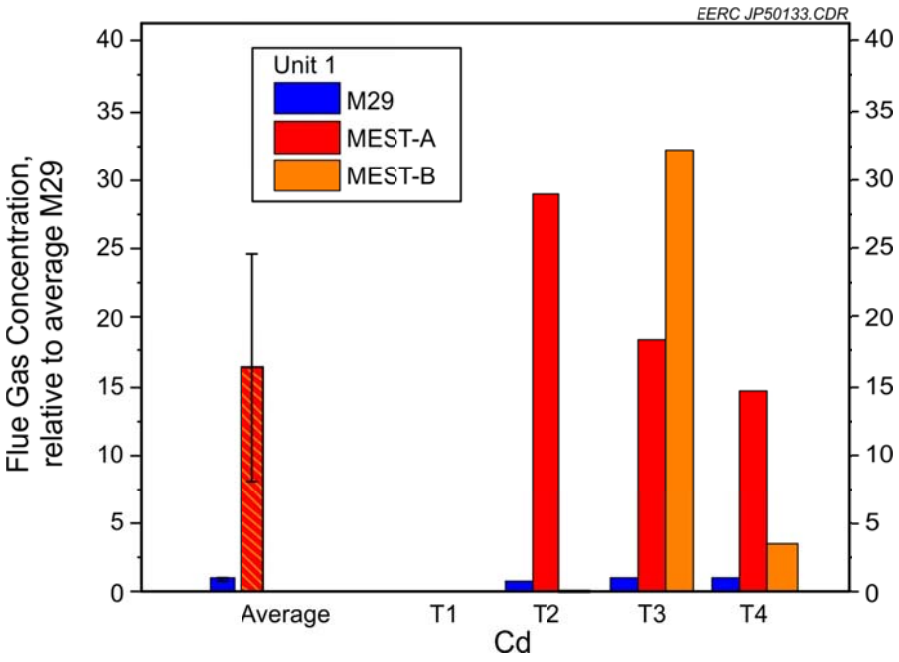

Figure D-7. Comparison of Cd between MEST-M and M29 (Unit 1).

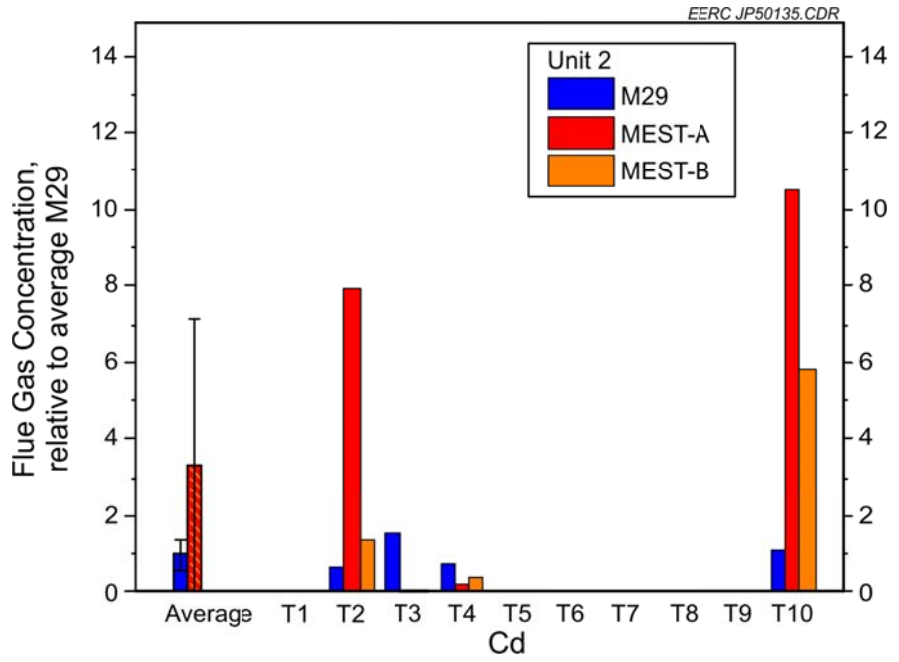

Figure D-8. Comparison of Cd between MEST-M and M29 (Unit 2).

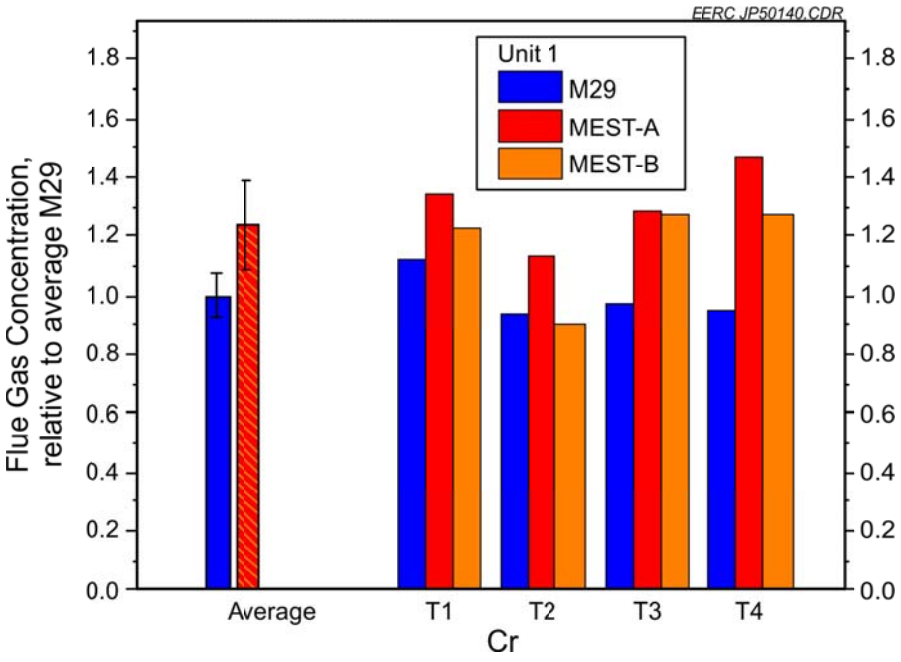

Figure D-9. Comparison of Cr between MEST-M and M29 (Unit 1).

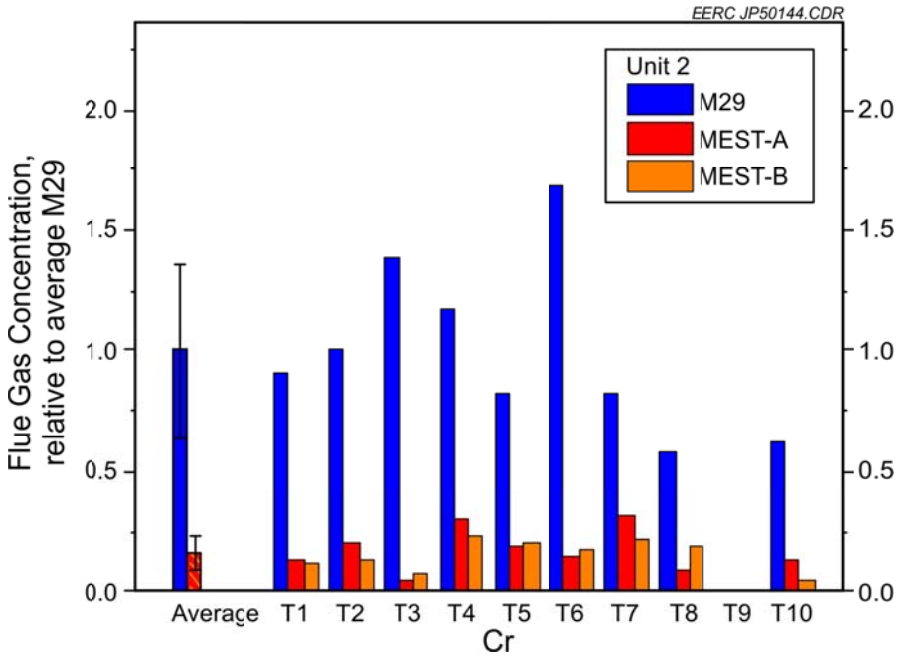

Figure D-10. Comparison of Cr between MEST-M and M29 (Unit 2).

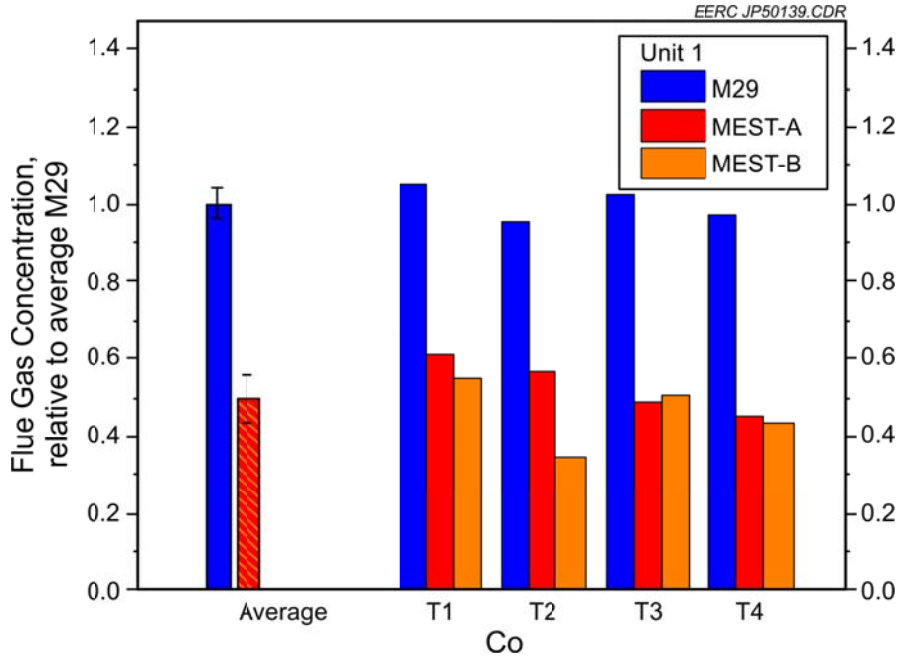

Figure D-11. Comparison of Co between MEST-M and M29 (Unit 1).

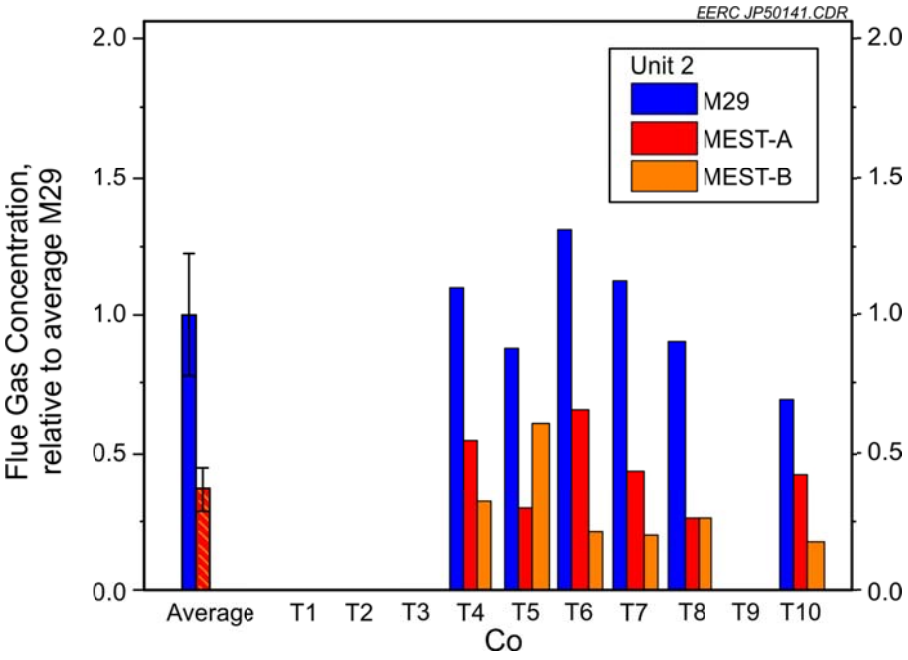

Figure D-12. Comparison of Co between MEST-M and M29 (Unit 2).

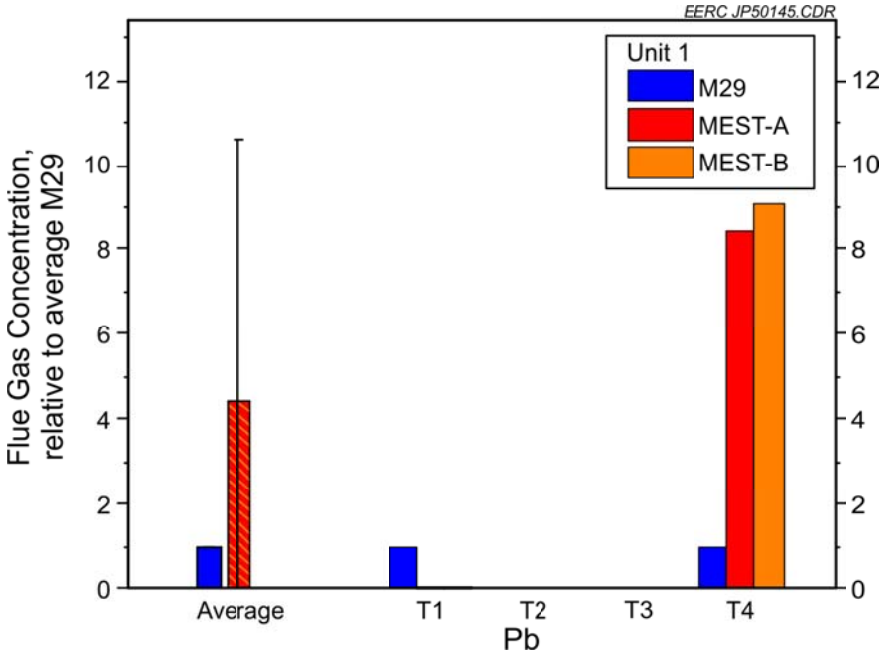

Figure D-13. Comparison of Pb between MEST-M and M29 (Unit 1).

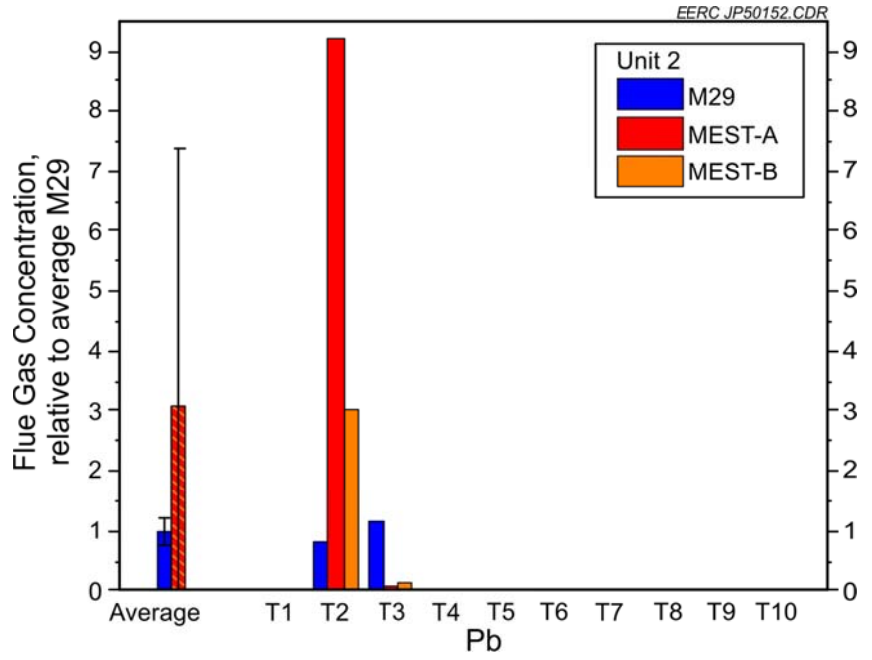

Figure D-14. Comparison of Pb between MEST-M and M29 (Unit 2).

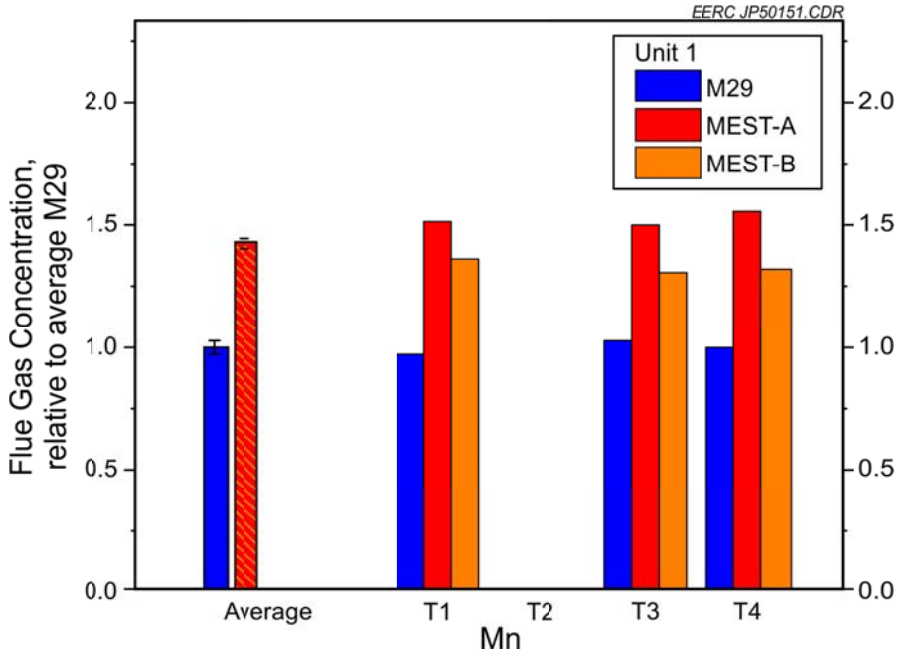

Figure D-15. Comparison of Mn between MEST-M and M29 (Unit 1).

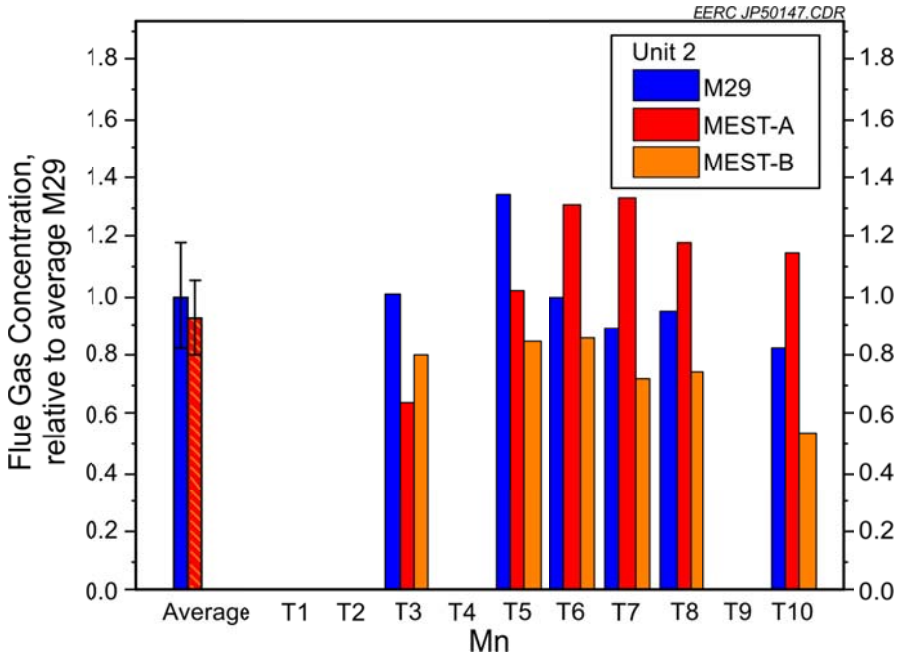

Figure D-16. Comparison of Mn between MEST-M and M29 (Unit 2).

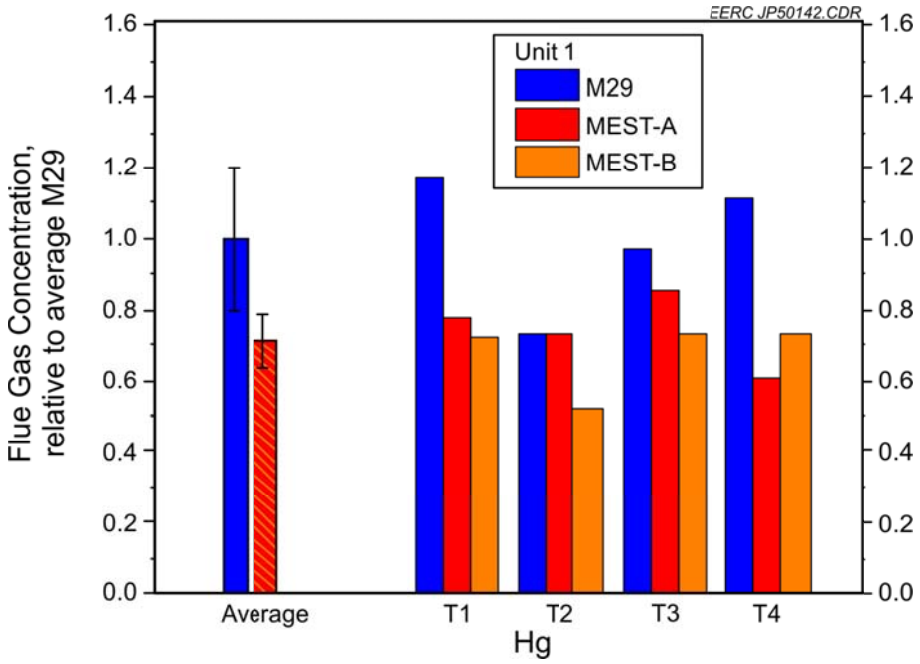

Figure D-17. Comparison of Hg between MEST-M and M29 (Unit 1).

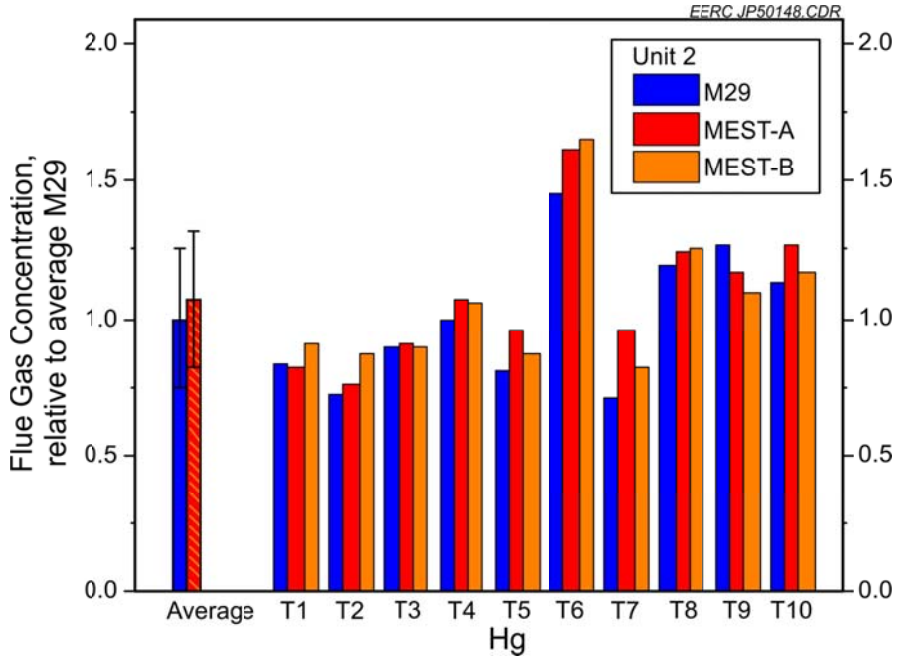

Figure D-18. Comparison of Hg between MEST-M and M29 (Unit 2).

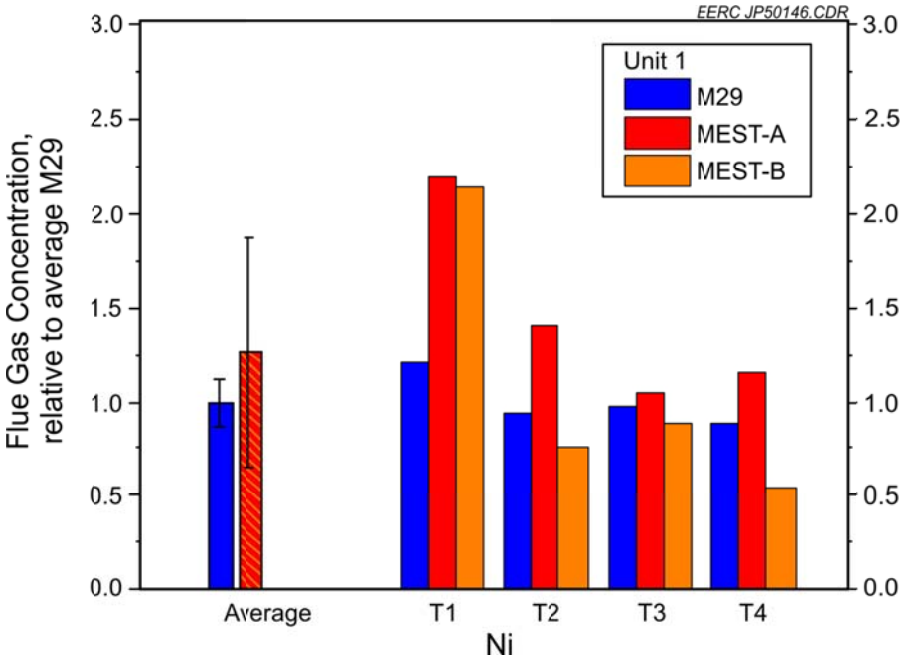

Figure D-19. Comparison of Ni between MEST-M and M29 (Unit 1).

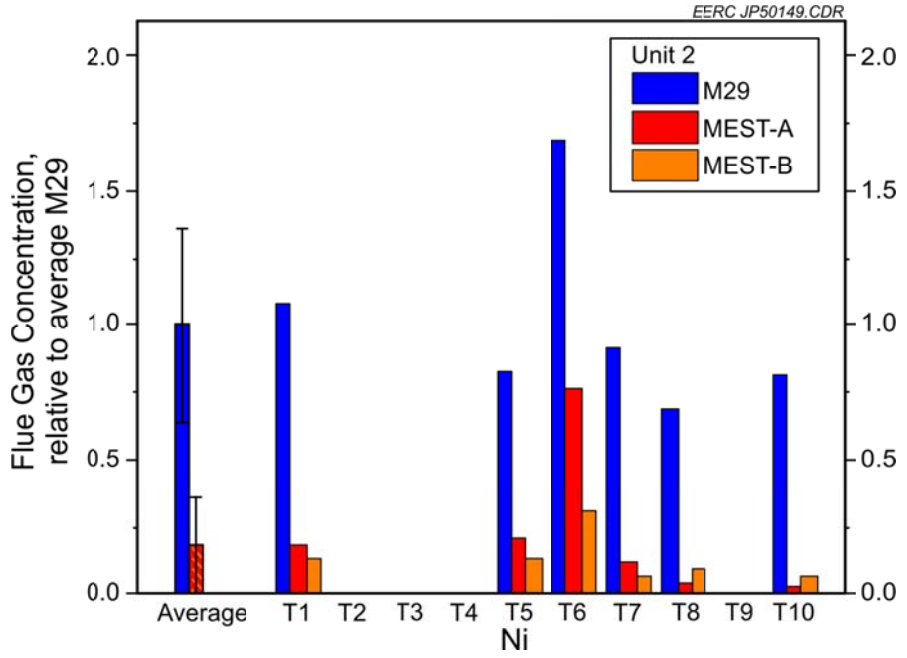

Figure D-20. Comparison of Ni between MEST-M and M29 (Unit 2).

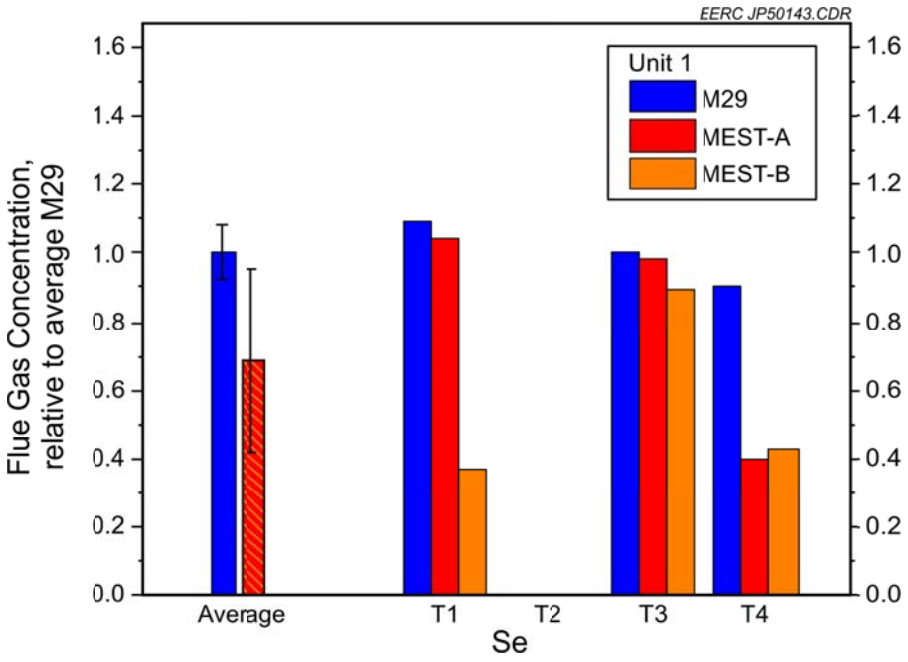

Figure D-21. Comparison of Se between MEST-M and M29 (Unit 1).

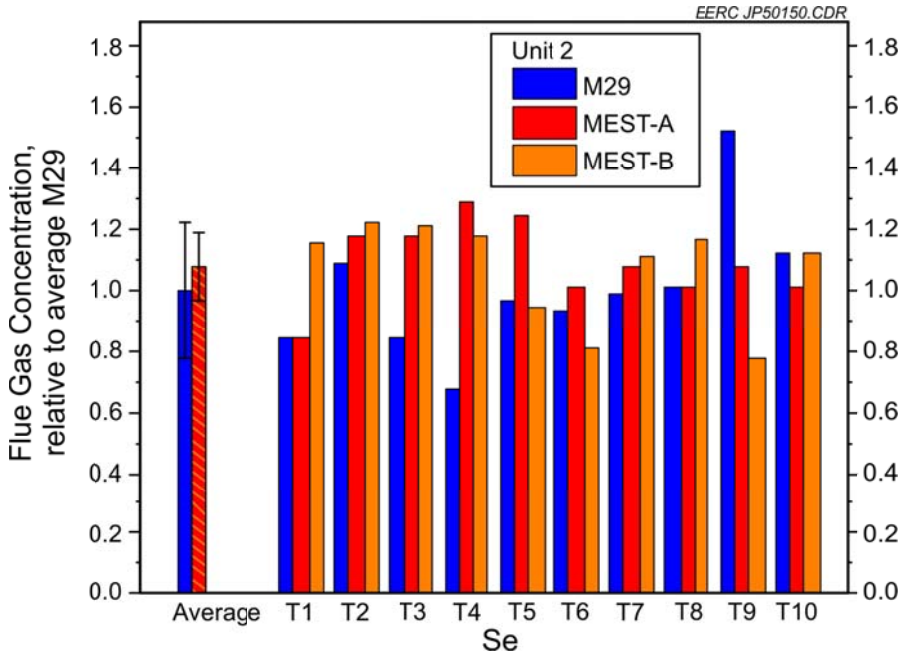

Figure D-22. Comparison of Se between MEST-M and M29 (Unit 2).

APPENDIX E

HALOGEN EMISSION RESULTS

Table E-1. Unit 1 U.S. Environmental Protection Agency Method 26A HCl Concentrations

		M26-1	M26-2	M26-3	M26-4	M26-5	M26-6	M26-7	M26-8	M26-9	M26-10	Average	RSD,[a] %
HCl	ppmvd[b]	43.7	46.9	42.8	45.1	46.2	44.5	43.3	43.1	42.9	44.1	44.3	3.2
HCl	lb/TBtu	50,136	53,782	49,162	51,744	53,079	51,065	49,720	49,530	49,223	50,589	50,803	3.2
HCl Removal	%	31.0	26.0	32.3	28.8	26.9	29.7	31.6	31.8	32.2	30.4	30.1	

[a] Relative standard deviation.
[b] Dry basis, at 3% O_2.
[c] Relative difference.

Table E-2. Unit 1 MEST-H (multielement sorbent trap-H) HCl Concentrations

		TM-1	TM-2	TM-3	TM-4	TM-5	TM-6	TM-7	TM-8	TM-9	TM-10	Average	RSD,[a] %
HCl	ppmvd[b]	43.3	45.5	41.7	43.3	42.9	42.0	41.1	43.1	40.5	41.8	42.5	3.3
HCl	lb/TBtu	49,749	52,212	47,844	49,670	49,197	48,264	47,204	49,522	46,451	47,955	48,807	3.3
HCl Removal	%	31.5	28.1	34.1	31.6	32.3	33.6	35.0	31.8	36.1	34.0	32.8	
Trap Pair	RD[c]%	1.6	1.1	1.0	0.4	1.7	0.2	0.9	2.1	0.1	2.2	1.2	
Spike Recovery	Rec., %	107.6		95.5					89.2		109.2	100.4	
O_2	%	5.0	4.9	4.9	5.0	5.0	4.9	4.9	4.8	4.9	5.0	4.9	
H_2O	%	9.8	7.1	9.9	9.9	10.1	9.4	10.1	10.6	9.5	8.9	9.5	
Stack Temperature	°F	357	355	358	355	357	353	361	356	353	360	357	

[a] Relative standard deviation.
[b] Dry basis, at 3% O_2.
[c] Relative difference.

Table E-3. Unit 2 U.S. Environmental Protection Agency Method 26A HCl Concentrations

	U4	M26-1	M26-2	M26-3	Average	RSD,[a] %
HCl	ppmvd[b]	1.1	0.6	1.7	1.2	45.8
HCl	lb/TBtu	1256	727	1915	1299	45.8
HCl Removal	%	98.8	99.3	98.1	98.7	

[a] Relative standard deviation.
[b] Dry basis, at 3% O_2.
[c] Relative difference.

Table E-4. Unit 2 MEST-H (multielement sorbent trap-H) HCl Concentrations

	U4	TM-1	TM-2	TM-3	Average	RSD,[a] %
HCl	ppmvd[b]	1.4	0.9	1.4	1.2	4.8
HCl	lb/TBtu	1564	988	1601	1384	24.8
HCl Removal	%	98.5	99.0	98.4	98.6	
Trap Pair	RD[c],%	29.5	9.1	2.2	13.6	
Spike Recovery	Recovery, %	46.2	40.4	91.3	59.3	
O_2	%	6.8	6.8	6.8	6.8	
H_2O	%	16.1	16.1	16.1	16.1	
Stack Temperature	F	132	132	132	132	

[a] Relative standard deviation.
[b] Dry basis, at 3% O_2.
[c] Relative difference.

Table E-5. Unit 1 U.S. Environmental Protection Agency Method 26A HBr Concentrations

	U123	M26-1	M26-2	M26-3	M26-4	M26-5	M26-6	M26-7	M26-8	M26-9	M26-10	Average	RSD,[a] %
HBr	ppmvd[b]	0.8	0.9	0.8	0.9	0.9	0.9	0.8	0.9	0.9	1.0	0.9	7.6
HBr	lb/TBtu	915	991	911	1045	1014	990	945	1076	994	1160	1004	7.6
HBr Removal	%	86.8	85.7	86.9	84.9	85.4	85.7	86.4	84.5	85.7	83.3	85.5	1.3

[a] Relative standard deviation.
[b] Dry basis, at 3% O_2.
[c] Relative difference.

Table E-6. Unit 1 MEST-H (multielement sorbent trap-H) HBr Concentrations

	U123	TM-1	TM-2	TM-3	TM-4	TM-5	TM-6	TM-7	TM-8	TM-9	TM-10	Average	RSD,[a] %
HBr	ppmvd[b]	1.2	1.2	1.3	1.2	1.2	1.3	1.3	1.2	1.3	1.3	1.3	4.1
HBr	lb/TBtu	1426	1371	1548	1423	1380	1455	1516	1422	1452	1518	1451	4.1
HBr Removal	%	79.4	80.2	77.7	79.5	80.1	79.0	78.2	79.5	79.1	78.1	79.1	1.1
Trap Pair	RD,[c]%	0.1	0.1	3.4	0.5	0.5	3.4	1.7	2.4	1.8	0.6	1.4	

[a] Relative standard deviation.
[b] Dry basis, at 3% O_2.
[c] Relative difference.

Table E-7. Unit 2 U.S. Environmental Protection Agency Method 26A HBr Concentrations

		M26-1	M26-2	M26-3	Average	RSD,[a] %
HBr	ppmvd[b]	1.0	0.8	0.9	0.9	12.3
HBr	lb/TBtu	1098	867	1060	1009	12.3
HBr Removal	%	94.9	96.0	95.1	95	0.6

[a] Relative standard deviation.
[b] Dry basis, at 3% O_2.
[c] Relative difference.

Table E-8. Unit 2 MEST-H (multielement sorbent trap-H) HBr Concentrations

		TM-1	TM-2	TM-3	Average	RSD,[a] %
HBr	ppmvd[b]	1.2	0.8	0.8	0.9	21.3
HBr	lb/TBtu	1318	917	940	1058	21.3
HBr Removal	%	93.9	95.7	95.6	95.1	1.1
Trap Pair	RD,[c] %	16.9	2.0	4.4	7.7	

[a] Relative standard deviation.
[b] Dry basis, at 3% O_2.
[c] Relative difference.

APPENDIX F

HALOGEN METHODS COMPARATIVE RESULTS

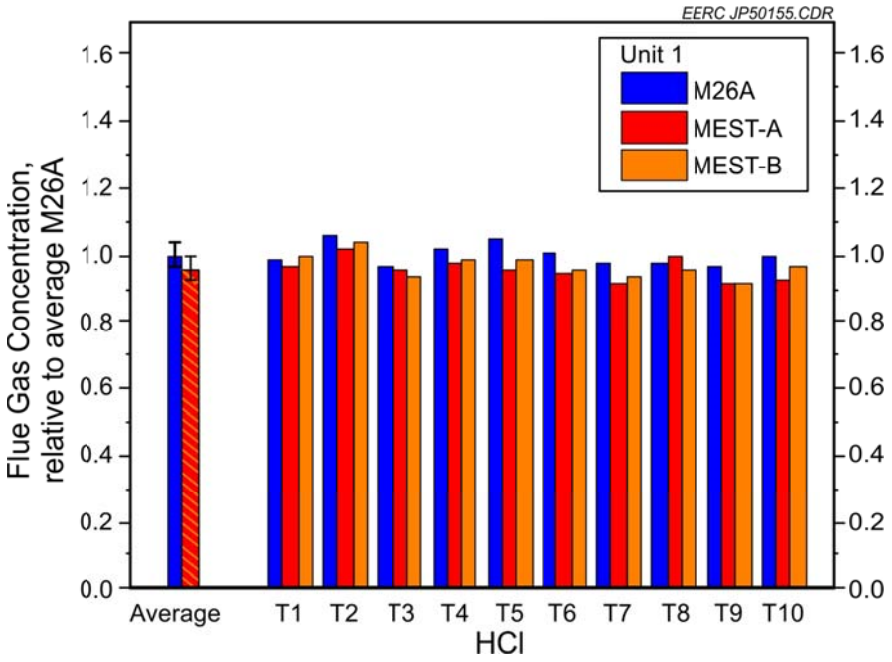

Figure F-1. Comparison of HCl between MEST-H and M26A (Unit 1).

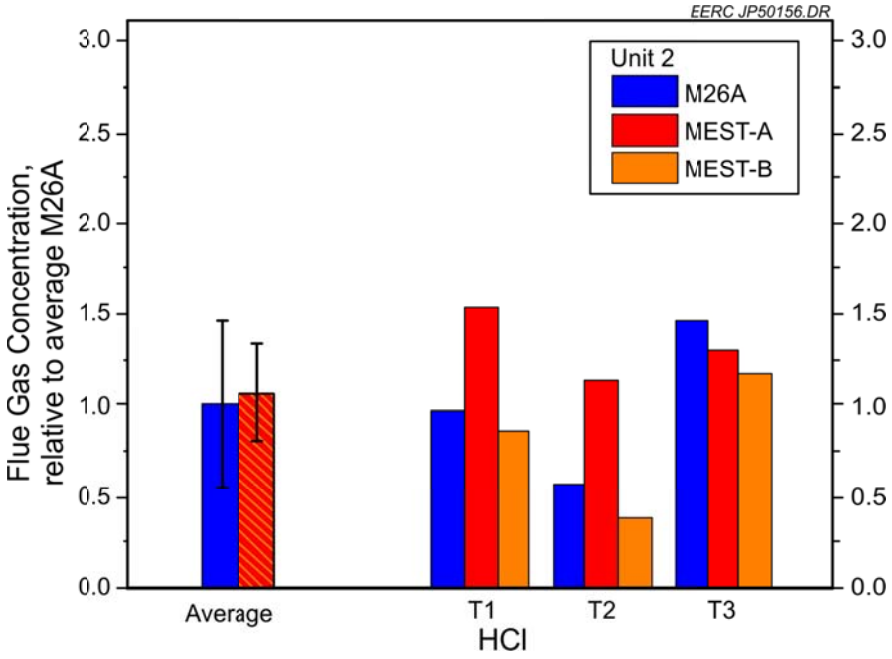

Figure F-2. Comparison of HCl between MEST-H and M26A (Unit 2).

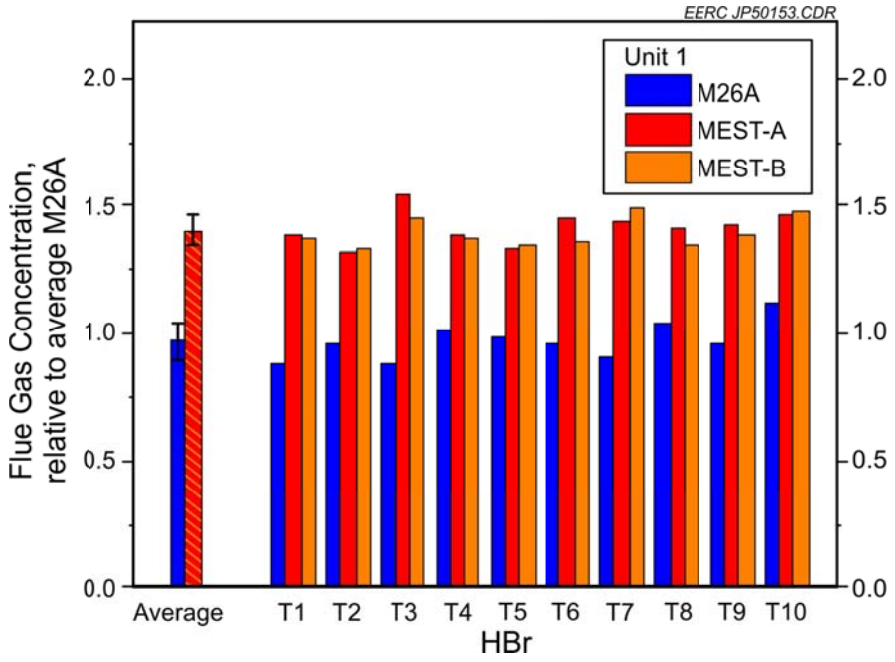

Figure F-3. Comparison of HBr between MEST-H and M26A (Unit 1).

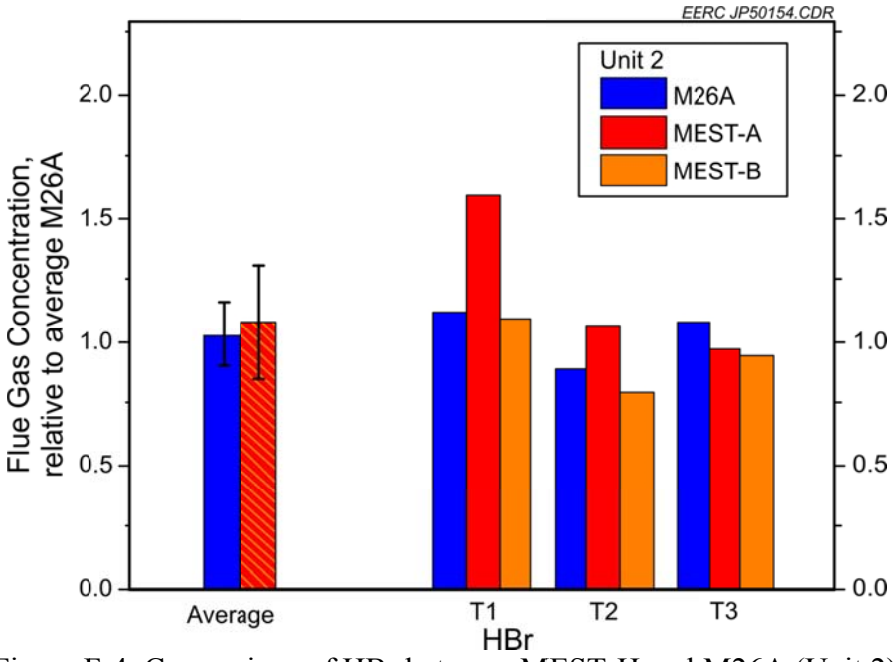

Figure F-4. Comparison of HBr between MEST-H and M26A (Unit 2).