Environmental Technology Verification Report

bm becker messtechnik gmbh
AMESA
(ADSORPTION METHOD FOR
SAMPLING DIOXINS AND FURANS)

Prepared by
Battelle

Battelle
The Business of Innovation

Under a cooperative agreement with

EPA **U.S. Environmental Protection Agency**

ETV ETV ETV

THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

ETV

EPA
U.S. Environmental Protection Agency

Battelle
The Business of Innovation

ETV Joint Verification Statement

TECHNOLOGY TYPE:	**Dioxin Emission Monitoring System**
APPLICATION:	**Monitoring Incinerator Emissions**
TECHNOLOGY NAME:	**Adsorption Method for Sampling Dioxins and Furans**
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The U.S. Environmental Protection Agency (EPA) has established the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies. Information and ETV documents are available at www.epa.gov/etv.

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

The Advanced Monitoring Systems (AMS) Center, one of six technology areas under ETV, is operated by Battelle in cooperation with EPA's National Exposure Research Laboratory. The AMS Center evaluated the performance of the bm becker messtechnik gmbh AMESA (Adsorption Method for Sampling Dioxins and Furans) in monitoring emissions of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). This verification statement provides a summary of the test results.

VERIFICATION TEST DESCRIPTION

The performance of the AMESA was evaluated in terms of relative accuracy (RA), range, data completeness, and operational factors (ease of use, maintenance, and consumables/waste generated). RA and range were determined by comparing AMESA results to those from reference samples collected simultaneously using Method 23 sampling trains. Range was determined from measurements over a variety of defined operating conditions that produced differing levels of PCDD/PCDFs. Data completeness was assessed as the percentage of maximum data return achieved by the AMESA over the test period. Operational factors were evaluated by means of operator observations and records of needed maintenance, vendor activities, and expendables used.

A 2.94 thousand British thermal unit per hour, 3-Pass Wetback Scotch Marine Package Boiler (SMPB), manufactured by Superior Boiler Works, Inc., and located at the EPA Research Triangle Park facility, was used for the verification test. During this verification test, the SMPB was fully instrumented with continuous emission monitors for a variety of species including dioxide, carbon monoxide, carbon dioxide, water, and hydrogen chloride. Reference samples were collected and analyzed for PCDD/PCDFs using Method 23 with several documented modifications.

QA oversight of verification testing was provided by Battelle and EPA. Battelle QA staff conducted a technical systems audit, a performance evaluation audit, and a data quality audit of 10% of the test data.

This verification statement, the full report on which it is based, and the test/QA plan for this verification test are all available at www.epa.gov/etv/centers/center1.html.

TECHNOLOGY DESCRIPTION

The following description of the AMESA is based on information provided by the vendor. This technology description was not verified in this test.

The AMESA long-term sampling apparatus is based on the isokinetic sampling of flue gas and the adsorption of PCDD, PCDF, and other persistent organic pollutants on an exchangeable adsorption-resin-filled cartridge. The AMESA system consists of a titanium sampling probe with probe shaft and heat exchanger, a cartridge unit as a collection point, and a control cabinet. The titanium probe is used for both the isokinetic sampling and cooling of the hot flue gas to less than 50°C. The cooled flue gas, together with any accumulated condensate, is fed into the cartridge filled with adsorption resin (XAD-2) via an upstream quartz wool filter. Flue gas conditions are monitored using sensors in the probe and are used by the control unit to adjust sampling rates to maintain isokineticity. The PCDD/Fs can be collected over a period of up to one month and then analyzed in a laboratory. All data required for the subsequent determination of the mass concentration are gathered automatically and stored on a static random access memory card.

VERIFICATION RESULTS

Parameter	Method of Evaluation	Results			
Accuracy	Comparison to Method 23 reference samples		**PCDDs**	**PCDFs**	**PCDD/Fs**
		RA Intermethod RSD Intramethod RSD	• 48.2% • 37.4% • 10.0%	• 49.0% • 20.9% • 8.4%	• 48.2% • 21.9% • 8.4%
Range	Percent difference comparison to Method 23 reference samples	• No dependence of accuracy on PCDD/F toxic equivalent (TEQ) over range of approximately 1 to 6 nanograms TEQ per dry standard cubic meter • No dependence of accuracy on sample duration over range of 4 to 16 hours			
Data completeness	Ratio of number of samples successfully collected to number of potential samples that could have been collected	100% completeness in number of samples collected			
Ease of use	Operator observations	• Installation of the AMESA system was completed by a representative of becker messtechnik within 48 hours • Effectively operated after 2 hours of training in basic operation • Installation of sampling media and removal of sampling media completed in approximately 15 minutes each[a] • Approximately 3% down time			
Maintenance		No maintenance was required.			
Consumables/waste generated		XAD-2 and glass wool were used in the sampling cartridges for sample collection. Methylene chloride, acetone, and toluene were used to rinse the probe liner and sampling tube.[a]			

[a] Installation and removal of sampling media were not typical of normal installation. The small duct diameter on the boiler required a special installation and included routine removal and rinsing of the probe liner and sampling line, which is not typically performed after each sampling period.

RSD = relative standard deviation

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Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

bm becker messtechnik gmbh AMESA (Adsorption Method for Sampling Dioxins and Furans)

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Notice

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

Foreword

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

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

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. Under a cooperative agreement, Battelle has received EPA funding to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/centers/center1.html.

Acknowledgments

Contents

Figures

Tables

List of Abbreviations

AMESA	Adsorption Method for Sampling Dioxins and Furans
AMS	Advanced Monitoring Systems
APCS	air pollution control system
CEM	continuous emission monitor
dscm	dry standard cubic meter
EMS	emission monitoring system
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
HW	hot/wet
LCD	liquid crystal display
NIST	National Institute of Standards and Technology
PCDD	polychlorinated dibenzo-p-dioxins
PCDF	polychlorinated dibenzofurans
PE	performance evaluation
QA	quality assurance
QC	quality control
QMP	quality management plan
RA	relative accuracy
RSD	relative standard deviation
RTP	Research Triangle Park
SRAM	static random access memory
SMPB	Scotch Marine Packaged Boiler
TEQ	toxic equivalent
TSA	technical systems audit

Chapter 1
Background

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

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

The EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of the bm becker messtechnik gmbh AMESA (Adsorption Method for Sampling Dioxins and Furans) in monitoring emissions of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF).

Chapter 2
Technology Description

The objective of the ETV AMS Center is to verify the performance characteristics of environmental monitoring technologies for air, water, and soil. This verification report provides results for the verification testing of the AMESA. Following is a description of the AMESA, based on information provided by the vendor. The information provided below was not verified in this test.

The AMESA (Figure 2-1) long-term sampling apparatus is based on the isokinetic sampling of flue gas and the adsorption of PCDD, PCDF, and other persistent organic pollutants on an exchangeable adsorption-resin-filled cartridge. The AMESA system consists primarily of three system components:

- Titanium sampling probe with probe shaft and heat exchanger
- Cartridge unit as a collection point
- Control cabinet.

The titanium probe is used for both the isokinetic sampling and cooling of the hot flue gas to less than 50°C. The cooled flue gas, together with any accumulated condensate, is fed into the cartridge filled with adsorption resin (XAD-2) via an upstream quartz wool filter.

Figure 2-1. Photograph of AMESA

Flue gas conditions are monitored using sensors in the probe and are used by the control unit to adjust sampling rates to maintain isokineticity.

The PCDD/Fs can be collected over a period of up to one month and then sent to a laboratory for analysis. The time required for sample analysis will vary depending on the method employed and the laboratory response time. For this verification test, AMESA cartridge samples were analyzed in the same

laboratory and by the same method as the reference samples collected during the test, and the rinsate samples were analyzed by an independent laboratory. All data required for the subsequent determination of the mass concentration are gathered automatically and stored on a static random access memory (SRAM) card.

The control cabinet consists of a

- Measuring gas cooler;
- Condensate collection container;
- Condensate pump;
- Filter with a condensate detector;
- Mass flow measuring device;
- Gas meter with a counting device and a temperature and pressure reading point; and
- Frequency converter and a rotary vane pump.

The control unit includes both menu-driven software and a process computer. The system is operated via five keys and a liquid crystal display (LCD) screen. This screen is also used to set parameters and retrieve important operational data. All data relevant for measurements is stored in the form of parameters which can be released only by means of a key switch. The computer monitors the function of all aggregates and registers all data required for the subsequent evaluation of the samples taken. At regular intervals, data are stored on an electronic data carrier (SRAM card). The SRAM card is later evaluated, together with the analysis results, to ascertain the mass concentration.

In addition to this ETV verification test, other evaluations of the AMESA system have been completed. The AMESA system was approved by the German Technical Inspection Authority (TÜV) in 1997, has received the MCerts certification in October 2005, and participated in a performance test for the Taiwanese EPA in 2001. During these tests many validation measurements against the respective standard methods (EN 1948, method 23 etc.) were done. The AMESA has also been deployed in approximately 100 applications. Results from these other tests and applications are available from the vendor.

Chapter 3
Test Design and Procedures

3.1 Introduction

EPA Method 23(1) is the certified extractive method used for quantifying PCDD/PCDF emissions from incinerators in the United States as well as in many other countries. This method is labor-intensive, expensive, and requires an extended time for subsequent laboratory analysis of collected samples. As a result, Method 23 measurements are made infrequently only for compliance purposes and not for long- or short-term performance monitoring. Emerging technologies are being developed to provide semi-continuous monitoring or long-term sampling of PCDD/PCDFs and may have the potential to provide more information on PCDD/PCDF source emissions than the relatively few samples required under federal or state regulations. For example, in Europe, mainly in Belgium and Germany, long-term sampling of PCDD/PCDFs has been used for compliance measurements since 2000. However, the performance of these newly introduced technologies has not been evaluated in the United States to determine their relative operational capabilities.

The purpose of this verification test was to generate performance data on the AMESA emission monitoring system. The test was conducted at EPA's Research Triangle Park (RTP), North Carolina, campus over a period of two weeks in September 2005 and was supported by ARCADIS under a subcontract from Battelle. The accuracy and range of the AMESA were determined through comparisons to a modified version of Method 23 for the integrated sampling of PCDD/PCDFs[1], with modifications as described in Section 3.2.2 of this report. Other performance parameters such as data completeness and operational factors were determined from operator observations.

This verification test was conducted according to procedures specified in the *Test/QA Plan for Verification of Dioxin Emission Monitoring Systems (EMSs),*[2] and the *Quality Management Plan (QMP) for the ETV/AMS Center.*[3] As described in this report, the performance of the AMESA was evaluated in terms of

- Relative accuracy (RA),
- Range,

- Data completeness, and
- Operational factors (ease of use, maintenance, and consumables/waste generated).

RA and range were determined by comparing AMESA results to those from reference samples collected simultaneously using Method 23 sampling trains. Range was determined from measurements over a variety of defined operating conditions that produced differing levels of PCDD/PCDFs. Data completeness was assessed as the percentage of maximum data return achieved by the AMESA over the test period. Operational factors were evaluated by means of operator observations and records of needed maintenance, vendor activities, and expendables used.

3.2 Experimental Setup

3.2.1 Test Facility

A 2.94 thousand British thermal unit per hour, 3-Pass Wetback Scotch Marine Package Boiler (SMPB), manufactured by Superior Boiler Works, Inc., and located at the EPA RTP facility, was used for the verification test. This boiler (Figure 3-1) is capable of firing natural gas or a variety of fuel oils. In this test, the oil burner was used; this burner is a low-pressure, air-atomizing nozzle that delivered a fine spray at an angle that ensured proper mixing with the air stream. The boiler has 33 square meters of heating surface and generates up to 1,090 kilograms per hour of saturated steam at pressures up to 15 pounds per square inch. Fuel flows were measured with a liquid volume totalizer, and stoichiometric ratios are verified through dioxide (O_2) and carbon dioxide (CO_2) emission concentrations.

Figure 3-1. Wetback Scotch Marine Package Boiler

During this verification test, the SMPB was fully instrumented with continuous emission monitors (CEMs) for a variety of species including O_2, carbon monoxide (CO), CO_2, water (H_2O), and hydrogen chloride (HCl). Continuous emission monitoring of chemical species was performed with two shared CEMs for the packaged boiler facility. One CEM bench included four gas analyzers: high-range CO, low-range CO, O_2, and CO_2. HCl was measured by a self-contained bench-scale CEM system (Bodenseewerk), which uses an Altech Hot/Wet (HW) sampling system and a Perkin-Elmer MCS-100 Infrared Multi-Component Analyzer. The MCS is capable of measuring up to eight compounds simultaneously, using gas filter correlation and single-beam dual-wavelength techniques. The HW probe assembly samples flue gases, while maintaining temperatures at elevated levels. The flue gas from the unit passes through a manifold to an air pollution control system (APCS) consisting of a natural-gas-fired secondary combustion chamber, a fabric filter, and an acid gas scrubber to ensure proper removal of pollutants. All

emission measurements are taken prior to the APCS. The SMPB facility was modified prior to testing to accommodate all the requirements of the verification test. These modifications included the addition of a section of duct equipped with several sampling ports at the exit of the boiler to allow for the simultaneous installation of multiple PCDD/PCDF EMSs and operation of duplicate Method 23 sampling trains. Figure 3-2 is a schematic illustration of the duct, identifying the sampling locations for the reference sample trains and the AMESA. As this figure shows, one Method 23 train sampled from a port upstream in the flue gas flow from the AMESA's sampling port, and the other sampled downstream.
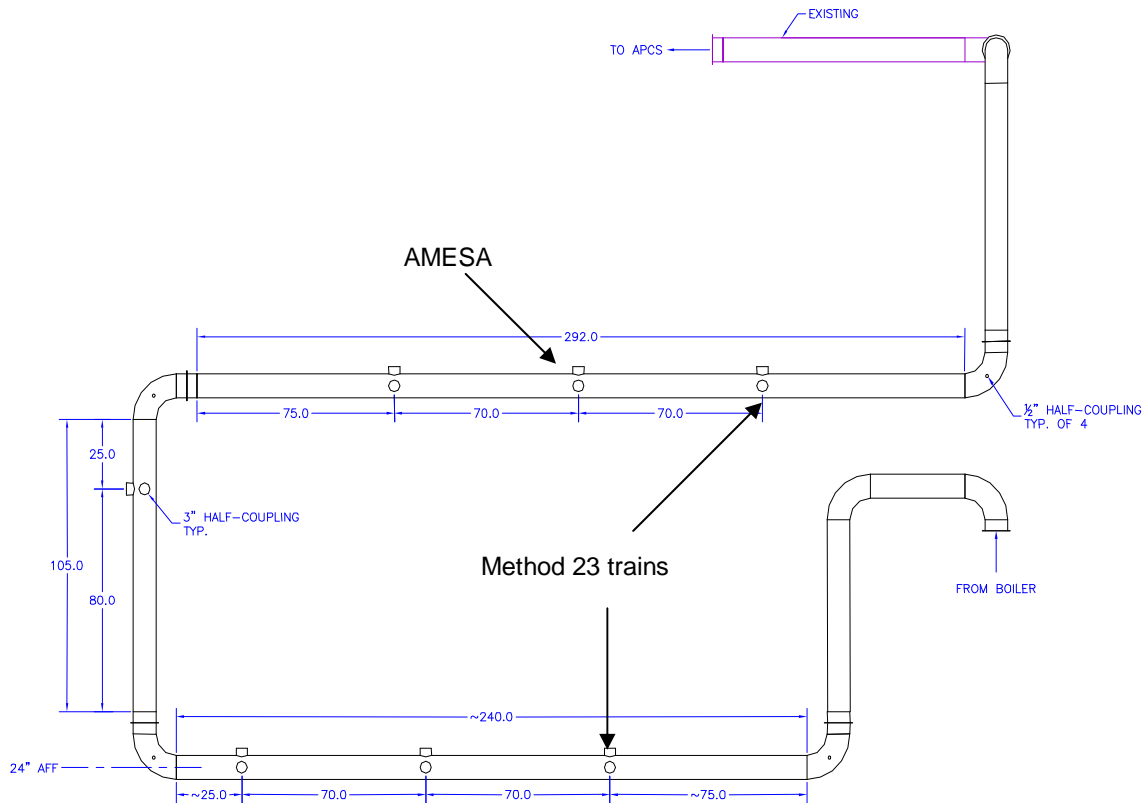
Figure 3-2. Illustration of Flue Gas Duct with Sampling Locations

A chlorinated chemical (1,2-dichlorobenzene) and a source of metal atoms (copper naphthenate) were added to the boiler fuel to promote PCDD/PCDF formation for the EMS testing.[4] A feed system was designed to safely tap the feed line to the fuel line just before the burner nozzle. The feed system consisted of a 37-liter pressurized stainless steel tank, in which the 1,2-dichlorobenzene and the copper naphthenate were mixed.

Values for the stack gas composition from the SMPB for each test run conducted during the verification test are presented in Section 6.1 of this verification report.

3.2.2 Reference Samples

Reference samples were collected and analyzed for PCDD/PCDFs using Method 23, with the following modifications established before any sample collection took place:

6

- Analysis was completed by high-resolution gas chromatography/low-resolution mass spectrometry.

- Mass locking was not used with low-resolution mass spectrometry.

- The front and back halves of the reference samples were extracted and analyzed together rather than separately.

- The internal and surrogate standards included several that were not required in the standard method.

- Extraction procedures called for in Method 23 were modified to allow more efficient extraction of mono- through tri-chlorinated PCDD/PCDFs.

ARCADIS collected the reference method samples and coordinated their analysis, which was conducted by EPA staff at the EPA RTP facility. To minimize potential bias caused by interlaboratory analysis differences, the AMESA samples were also analyzed by EPA staff. EPA staff ensured that the analytical instrumentation was calibrated and the samples were analyzed according to the requirements of the modified Method 23 and that the appropriate QA/quality control (QC) activities were conducted according to the method. Records of all calibrations and sample analyses were provided to Battelle and are maintained in the test files. Additionally, rinsate samples from the probe liners and sampling lines from the AMESA were collected and analyzed by an independent contract laboratory. The results of those analyses were combined with the results of the AMESA samples analyzed at the EPA laboratory to generate the final results presented in this report.

3.2.2.1 Reference Sample Collection

As shown in Figure 3-2, the Method 23 samples were collected at the two extreme locations of the stack gas sampling section, to bracket the locations of the technologies being evaluated in this verification test. The reference method sampling included pre-spiking the XAD-2 traps with carbon-13 labeled PCDD/F pre-sampling surrogates. Both sampling trains consisted mainly of a heated probe, heated box containing a cyclone and a filter, water-cooled condenser, water-cooled XAD-2 cartridge, impinger train for water determination, leak-free vacuum line, vacuum pump, and a dry gas and orifice meter with flow control valves and vacuum gauge. Temperatures were measured and recorded in the hot box (set at 125°C), at the impinger train outlet, at the XAD-2 cartridge outlet (maintained to be below ambient temperature), and at the inlet and outlet of the dry gas meter. Leak checks were conducted at the beginning and end of each sample run. Prior to sampling, all glassware, probe materials, glass wool, and aluminum foil were cleaned following the Method 23 cleaning procedure.

3.2.2.2 Sample Recovery

Following completion of each test run, each sampling train was recovered in a clean area, and the cleanup procedure began as soon as the probe was removed from the sample source location. During the transportation between the test facility and the designated recovery area, both ends of the heated probe and openings of the impinger assembly were sealed with aluminum foil or glass caps.

The front-half and back-half trains were recovered separately but analyzed together since no gas/solid phase PCDD/F speciation was required for this verification test. The probe and front half of the filter housing for each sample train were rinsed with acetone followed by dichloromethane and the rinsate was collected in a single 250-milliliter (mL) amber jar. The probe and front-half filter housing were then rinsed with toluene and the rinsate was collected in a separate 250-mL amber jar. The filter was recovered and placed in a Petri dish sealed with Teflon tape.

The back-half sample train, which consisted of an XAD-2 cartridge, the back-half filter housing, glass connection, and condenser, were recovered separately. The XAD-2 resin cartridge from each train was capped at both ends and wrapped in aluminum foil during transport. As with all sample fractions, the XAD-2 resin cartridges remained refrigerated during storage and transport. The back-half glassware was rinsed and the rinsate was collected in the same way as the front-half rinses. The solvent rinse jars for both the front- and back-half sample trains were capped with Teflon-lined caps, sealed with Teflon tape to prevent leakage, and stored in a refrigerated space before being sent for analysis.

3.2.3 AMESA Installation and Operation

Figure 3-3 shows the installation of the AMESA sampling unit on the duct. Since the diameter of the exhaust duct was considerably smaller than normal full-scale applications, the installation of the AMESA probe was modified from the normal configuration. The modified installation required a section of unheated Teflon tubing (approximately 1 meter in length) to deliver the sample gas from the exit of the probe to the sampling media. Because of the potential for loss of PCDD/F in this unheated line, the rinsate samples noted in Section 3.2.2 were collected and analyzed. It should be noted that the connection between the rigid Teflon and the metal probe liner is known to be a potential source for leaking, especially when nothing additional (such as a tapping clip or sealing tape) is used to secure the tubing to the metal. A leak test was performed according to the EPA method prior to and after each test run but did not include the Teflon tubing part of the train. A continuous leak check of the sampling train was not performed. Leaks in the sampling train could potentially result in sample volumes that are biased high and consequently reported analyte concentrations biased low relative to actual flue gas concentrations. Although no attempt was made in this verification test to determine if there were leaks of this type, in the standard AMESA installation the connections are made using a sealed thread and a small clamped flange, which assures good sealing and minimizes leaks in the sampling train.

Figure 3-3. Installation of AMESA Sampling Probe

Figure 3-4. AMESA Control Unit

Immediately prior to each test run, a sampling cartridge was installed in the AMESA sampling unit and an empty data card was installed in the control unit. During the verification test, the AMESA system was manually started and stopped for each test run, although the AMESA allows for automated operation. After completion of each test run, the sampling cartridge, probe liner, and tubing leading from the probe to the sampling unit were removed. The probe liner and tubing were rinsed with methylene chloride and then with toluene. The rinsate and sampling cartridges were stored in a freezer until transport to their respective laboratories for analysis.

Figure 3-4 shows the control unit of the AMESA system which was located approximately 10 meters from the sampling unit.

3.3 Test Design

RA, range, data completeness, and operational factors for the AMESA were evaluated.

3.3.1 Relative Accuracy

The RA of the AMESA was evaluated by comparing its results to simultaneous results obtained by reference samples of the flue gas collected using Method 23. During the verification test, a series of nine Method 23 test runs were conducted using duplicate Method 23 trains. The Method 23 trains sampled from ports located at each end of the sampling region where the AMESA was installed, as shown in Figure 32. The reference samples were recovered and submitted for analysis by the modified version of Method 23 described in Section 3.2. The PCDD/PCDF concentrations determined by the reference methods were compared to corresponding results from the AMESA, averaged over the period of each Method 23 test run. During each of the test runs, the boiler operation was maintained as constant as possible. However, the duration of the sampling periods and the operating conditions of the boiler were changed from run to run to provide a range of conditions under which the AMESA was evaluated. Two sets of operating conditions were used for the test runs to generate expected high (i.e., 5-10 ng TEQ/dscm) and low (i.e., 1-2 nanograms [ng] toxic equivalent [TEQ]/dry standard cubic meter [dscm]) PCDD/PCDF concentrations. Test runs of various durations were conducted under each set of operating conditions. Sampling periods of four hours were used to assess short-term accuracy, whereas long-term accuracy was assessed from composite samples collected over two 8-hour sampling periods on successive days (i.e., totaling 16 hours per sample). Table 3-1 shows the sampling durations and boiler operating conditions for each of the nine test runs. Two Method 23 trains were used to collect each reference sample during each test run. These trains sampled isokinetically from a single point in the gas flow, with one of the trains sampling at each end of the sampling region.

Upon completion of each test run, the Method 23 trains were dismantled for sample recovery in the field by ARCADIS staff, and all collected sample fractions were logged and stored for transfer to the analytical laboratory. Subsequent to analysis, ARCADIS reviewed the data and reported final PCDD/F concentrations from all trains in units of TEQ/dscm, corrected to 7% O_2. The results from the simultaneously collected Method 23 trains were used to assess the degree of PCDD/F loss (if any) in the duct between the two reference method sampling ports. Unless discrepancies of greater than 30% were observed between the reference samples collected simultaneously for total measured TEQs, the results from the reference method samples were averaged together to produce the final reference data used for comparison to the AMESA results. If discrepancies of greater than 30% were observed, the data were flagged and the samples treated as independent samples for comparison to the AMESA.

Table 3-1. Test Run Summary

Date	Test Run	Sampling Duration	Expected PCDD/PCDF Concentration[a]
9/12/05	1	4 hours	Low
9/13/05	2	4 hours	Low
9/14/05 & 9/15/05	3,4	16 hours (2 x 8 hours)	High
9/16/05	5	4 hours	High
9/17/05	6	4 hours	High
9/18/05 & 9/19/05	7, 8	16 hours (2 x 8 hours)	Low
9/20/05	9	8 hours	High

[a] Expected concentrations based on results of baseline testing. "High" corresponds to expected total PCDD/F TEQ of roughly 5-10 ng TEQ/dscm, and "low" corresponds to expected concentrations of roughly 1-2 ng TEQ/dscm.

3.3.2 Range

Range was assessed in terms of RA over the range of measured PCDD/PCDF concentrations and sampling periods. The reference method samples were collected over a range of expected PCDD/F concentrations to assess the degree of agreement of the AMESA with the reference method. Based on results from baseline testing of the boiler conducted prior to the verification test, the dopant injection rate and firing conditions were changed for different test runs to achieve different expected PCDD/F concentrations (i.e., high or low concentration). Additionally, the duration of the test runs was varied to achieve a range of sampling periods from 4 to 16 hours. During each test run, the flue gas HCl level was used as an indicator of the expected PCDD/F concentrations in the flue gas, and the dopant injection rate was varied to achieve different expected PCDD/F levels for the test runs.

3.3.3 Data Completeness

Data completeness was assessed based on the overall data return achieved by the AMESA. It was reported as the percentage of acceptable samples collected during the verification test out of the total number of test runs and as the percentage of time that the AMESA system was collecting samples relative to the total duration of test runs.

3.3.4 Operational Factors

Operational factors such as maintenance needs, data output, consumables used, ease of use, and repair requirements were evaluated based on observations recorded by Battelle and facility staff, and in some cases by the vendor. A laboratory record book maintained at the test facility was used to enter daily observations on these factors.

Chapter 4
Quality Assurance/Quality Control

QA/QC procedures were performed in accordance with the QMP for the AMS Center[3] and the test/QA plan[2] for this verification test.

4.1 Audits

4.1.1 Performance Evaluation Audits

A performance evaluation (PE) audit was conducted to assess the quality of the critical measurements associated with the reference sampling and analysis methods. In the PE audit, critical measurements were checked by comparing them with appropriate National Institute of Standards and Technology (NIST)-traceable standards, when available. Table 4-1 shows the critical measurements that were audited, the audit procedures and acceptance criteria for the audit comparisons, and the audit results. An initial PE audit of the Method 23 gas flow rate did not meet the acceptance criterion. However, the flow transfer standard used for the audit was found to be working improperly and therefore not appropriate for comparison. The audit was repeated using a different flow transfer standard. The results of the second audit are presented in the table.

The PE audit of the internal standard recovery was performed by spiking one blank Method 23 train with an NIST-traceable PCDD/PCDF solution, provided by Battelle, and independent of the internal standards used for the reference method samples. The spiked train was not used to collect a flue gas sample, but was recovered and analyzed in the same manner as the other Method 23 trains; and the analytical results were compared with the spike amount to assess recovery. The target criteria for this PE audit were 40% to 130% recovery of the internal standards for the tetra- through hexachlorinated compounds and 25% to 130% for the hepta- and octachlorinated compounds. The actual recoveries were well within these limits, ranging from 101% to 120% for all compounds.

Table 4-1. Methods and Acceptance Criteria for PE Audit Measurements

Critical Measurement	PE Audit Method	Acceptance Criteria	Audit Results
Method 23 gas sample flow rate	Compare to independent flow measurement device	±5%	2.2 %– 3.4% Pass
Method 23 stack gas temperature	Compare to independent temperature measurement device	±2% absolute temperature	0.0% – 0.55% Pass
Barometric pressure	Compare to independent pressure gauge	±1% absolute pressure	0.4% Pass
PCDD/PCDF internal standard recovery	Method spike with an independent PCDD/PCDF standard	40% to 130% for tetra- through hexachlorinated compounds; and 25% to 130% for hepta- and octachlorinated compounds	101% – 120% Pass
PCDD/PCDF surrogate standard recovery	Field spike with an independent PCDD/PCDF standard	70% to 130% recovery	91% – 107% Pass

The PE audit of the surrogate standard recovery was performed by spiking one blank XAD-2 cartridge with an NIST-traceable PCDD/PCDF surrogate standard solution provided by Battelle, and independent of the surrogate standards used for the reference method samples. This spiked cartridge was extracted and analyzed in the same manner as the other cartridges. The target criterion for this PE audit was 70% to 130% recovery of the surrogate standards. The actual recoveries were well within these limits, ranging from 91% to 107% for all compounds.

4.1.2 Technical Systems Audits

The Battelle Quality Manager performed a technical systems audit (TSA) on September 13 and 14, 2005, to ensure that the verification test was being performed in accordance with the AMS Center QMP,[3] the test/QA plan,[2] published reference methods, and any standard operating procedures used by the test facility. In the TSA, the Battelle Quality Manager toured the test site, observed Method 23 sampling and sample recovery, inspected documentation of reference sample chain of custody, and reviewed laboratory record books. The Quality Manager also checked standard certifications and Method 23 data acquisition procedures. A TSA report was prepared, including a statement that no significant findings or corrective actions were identified.

A single deviation from the test/QA plan was documented as a result of the TSA. This deviation involved differences between the extraction procedures used by the EPA laboratory and the procedures in Method 23. The EPA laboratory used modified procedures that allowed for the extraction and quantification of lower chlorinated PCDD/PCDFs (e.g., mono- through trichlorinated PCDD/PCDFs). The modified procedures did not impact the quality of the data for this verification test.

Additionally, the EPA AMS Center Quality Officer conducted a TSA on September 14, 2005. There were no significant findings or correctives identified during that audit.

4.1.3 Audit of Data Quality

At least 10% of the data acquired during the verification test were audited. Battelle's Quality Manager, or designee, traced the data from the initial acquisition, through reduction and statistical analysis, to final reporting, to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit were checked.

4.2 Quality Assurance/Quality Control Reporting

Each assessment and audit was documented in accordance with Section 3.3.4 of the QMP for the ETV AMS Center.[3] Once the assessment report was prepared, the Battelle Verification Test Coordinator ensured that a response was provided for each adverse finding or potential problem and implemented any necessary follow-up corrective action. The Battelle Quality Manager ensured that follow-up corrective action was taken. The results of the TSA were sent to the EPA.

4.3 Data Review

Data generated during this test were reviewed by a Battelle technical staff member within two weeks of generating the data. The reviewer was familiar with the technical aspects of the verification test, but was not the person who generated the data. The person performing the review added his/her initials and the date to a hard copy of the record being reviewed.

Chapter 5
Statistical Methods and Reported Parameters

The statistical methods presented in this chapter were used to verify the RA, range, and data completeness of the AMESA during this verification test.

5.1 Relative Accuracy

The RA of the AMESA with respect to the reference sample results was assessed as a percent bias, using Equation (1):

$$RA = \frac{\left(\left| \bar{d} \right| + t_{0.975} \frac{S_d}{\sqrt{n}} \right)}{\overline{RM}} \times 100 \qquad (1)$$

where

$\left| \bar{d} \right|$ = the absolute value of the mean of the differences between the AMESA and reference sample results for each test run,

$t_{0.975}$ = the one-tailed t-value for the 97.5% confidence level,

S_d = the standard deviation of the differences between the AMESA and reference sample results for each test run, and

$\overline{RM}$ = the mean of the reference method results.

In addition to the RA, the intermethod relative standard deviation (RSD) was also calculated according to Equation (2):

$$RSD = \sqrt{\frac{\sum_{i=1}^{n} \left(\frac{SD_i}{X_i} \right)^2}{n^2}} \qquad (2)$$

where

$SD_i =$ the standard deviation of the paired AMESA and reference method results for test run i,

$X_i =$ the average of the paired AMESA and reference method results for test run i, and

$n =$ the number of test runs.

The intramethod RSD was also calculated using Equation (2) where the standard deviations and averages were calculated from the duplicate reference method results for each test run.

5.2 Range

The range of the AMESA is reported in terms of its bias relative to the reference method, expressed both as a percent difference and absolute difference, under the variety of boiler operating conditions and sampling durations used during the test runs.

5.3 Data Completeness

Data completeness was calculated as the percentage of the total possible data return over the entire field period. The cause of any substantial incompleteness of data return was established from operator observation or vendor records and noted in the discussion of data completeness results.

5.4 Operational Factors

Operational factors were evaluated based on operator observations. No statistical comparisons of operational factors were made.

Chapter 6
Test Results

The results of the verification test of the AMESA are presented below for each of the performance parameters. Test runs were designed to be either 4- or 8-hour periods at high or low PCDD/F concentrations. Table 6-1 presents a summary of the test runs that were completed during the verification test along with a summary of the flue gas conditions.

Table 6-1. Summary of Test Runs and Testing Conditions

Test Run	Date	Duration (hours)	Expected PCDD/F Conc.	Stack Temp. (^{o}F)	O_2 Conc. (%)	CO_2 Conc. (%)	H_2O Conc. (%)
1	9/12/2005	4	Low	312.0	4.28	12.85	8
2	9/13/2005	4	Low	313.5	4.72	12.77	8
3	9/14/2005[a]	8	High	305.5	4.30	12.98	8
4	9/15/2005[a]	8	High	309.5	5.38	12.22	10
5	9/16/2005	4	High	319.0	5.04	12.31	8
6	9/19/2005	4	High	316.5	5.09	12.23	8
7	9/20/2005[a]	8	Low	303.0	4.8	12.36	8
8	9/21/2005[a]	8	Low	305.5	3.12	13.35	8
9	9/22/2005	8	High	315.5	3.38	13.04	8

[a] The samples for Test Runs 3 and 4 and 7 and 8 were collected on a single cartridge for the AMESA and analyzed as a single 16-hour test run.

Table 6-2 lists the reference method results for each test run. The results are presented for the modified Method 23 samples that were collected at the first sampling port (Port 1) and the seventh sampling port (Port 7). The top portion of the table shows the readings for individual PCDD/PCDF congeners. The lower portion of the table summarizes the toxic equivalent (TEQ) values for each test run according to PCDDs, PCDFs, and the total. All results were corrected to 7% O_2.

17

Table 6-2. Reference Modified Method 23 Results

Compound	Concentration [ng/dscm @ 7% O_2]																	
	Test Run 1		Test Run 2		Test Run 3		Test Run 4		Test Run 5		Test Run 6		Test Run 7		Test Run 8		Test Run 9	
	Port 1	Port 7	Port 1	Port 7	Port 1	Port 7	Port 1	Port 7	Port 1	Port 7	Port 1	Port 7	Port 1	Port 7	Port 1	Port 7	Port 1	Port 7
2,3,7,8 - TeCDD	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
1,2,3,7,8 - PeCDD	0.2	0.2	0.1	0.1	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.1	0.1	0.1	0.0	0.1	0.1
1,2,3,4,7,8 - HxCDD	0.1	0.1	0.1	0.1	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.2	0.2
1,2,3,6,7,8 - HxCDD	0.1	0.1	0.1	0.1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.2	0.1	0.1	0.1	0.1	0.2	0.2
1,2,3,7,8,9 - HxCDD	0.1	0.1	0.0	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.1	0.0	0.0	0.1	0.1	0.1
1,2,3,4,6,7,8 - HpCDD	0.5	0.5	0.4	0.4	1.6	1.8	2.0	2.0	1.8	1.4	1.4	1.3	0.4	0.4	0.3	0.4	1.0	1.1
1,2,3,4,6,7,8,9 - OCDD	0.8	0.8	0.7	0.6	3.0	3.3	4.6	4.5	3.2	2.6	3.1	2.8	0.7	0.6	0.5	0.6	1.8	1.8
2,3,7,8 - TeCDF	0.7	0.6	0.4	0.4	2.5	2.5	2.0	2.3	1.8	1.6	1.6	1.4	0.4	0.4	0.2	0.2	1.6	1.5
1,2,3,7,8 - PeCDF	0.8	0.8	0.6	0.5	3.2	3.4	2.9	3.4	3.0	2.4	2.3	2.2	0.6	0.6	0.4	0.4	2.1	2.0
2,3,4,7,8 - PeCDF	1.8	1.8	1.3	1.1	6.8	7.2	6.2	7.1	6.5	5.2	5.4	4.9	1.3	1.2	1.0	0.9	4.6	4.4
1,2,3,4,7,8 - HxCDF	1.6	1.6	1.2	1.1	6.1	6.8	6.5	7.3	7.2	5.7	5.7	5.3	1.6	1.5	1.2	1.2	4.5	4.6
1,2,3,6,7,8 - HxCDF	1.1	1.2	0.9	0.8	4.8	5.3	4.9	5.6	5.4	4.2	4.3	4.1	1.2	1.1	0.9	0.9	3.4	3.4
2,3,4,6,7,8 - HxCDF	0.9	0.9	0.6	0.5	3.3	3.7	3.2	3.8	3.6	2.7	3.0	2.8	0.8	0.7	0.6	0.6	2.3	2.3
1,2,3,7,8,9 - HxCDF	0.1	0.1	0.0	0.0	0.3	0.3	0.2	0.3	0.3	0.2	0.2	0.2	0.1	0.1	0.1	0.0	0.2	0.2
1,2,3,4,6,7,8 - HpCDF	3.2	3.5	2.6	2.4	12.7	13.7	15.9	16.7	15.5	12.2	13.3	12.5	3.7	3.4	2.7	2.8	9.6	9.7
1,2,3,4,7,8,9 - HpCDF	0.4	0.5	0.3	0.3	2.0	2.2	2.1	2.2	2.1	1.6	1.4	1.4	0.4	0.3	0.3	0.3	1.4	1.5
1,2,3,4,6,7,8,9 - OCDF	1.0	1.3	0.9	0.9	6.2	6.5	8.6	7.9	6.7	5.3	4.8	4.5	1.1	1.0	0.9	0.8	4.3	4.1
	Concentration[a][ng TEQ /dscm @ 7% O_2]																	
Total PCDD TEQ	0.22	0.23	0.17	0.14	0.42	0.46	0.42	0.44	0.42	0.35	0.31	0.29	0.11	0.10	0.10	0.07	0.23	0.25
Total PCDF TEQ	1.41	1.39	1.03	0.88	5.39	5.76	5.13	5.82	5.41	4.28	4.43	4.08	1.13	1.07	0.83	0.81	3.71	3.60
Total PCDD/F TEQ	1.63	1.62	1.19	1.01	5.81	6.22	5.55	6.26	5.84	4.63	4.74	4.37	1.24	1.17	0.93	0.87	3.94	3.85

[a] TEQ values calculated using the WHO 98 TEF values.

The TEQ values for each test run are also presented in Table 6-3, along with the calculated percent difference between the results from the two Method 23 trains. With the exception of the TEQ results for PCDD/PCDFs in Test Run 8, the results from the two trains are within 30%, indicating no substantial biases based on the sampling port locations. Even for Test Run 8, the large relative difference observed for the PCDDs originates because of the low absolute concentrations of PCDDs in that run. Since the PCDFs for that test run agree well for the two trains, indicating that there was no substantial bias between the ports for that run, so the average of the results was used in all cases for evaluation of the AMESA.

Table 6-3. Results from the Modified Method 23 Reference Samples

Test Run	PCDD TEQ			PCDF TEQ			Total PCDD/F TEQ		
	Port #1	Port #7	% Diff.	Port #1	Port #7	% Diff.	Port #1	Port #7	% Diff.
1	0.22	0.23	-5.5%	1.41	1.39	0.3%	1.63	1.62	0.6%
2	0.17	0.14	17.7%	1.03	0.88	16.1%	1.19	1.01	16.4%
3	0.42	0.46	-7.5%	5.39	5.76	-6.8%	5.81	6.22	-6.8%
4	0.42	0.44	-5.3%	5.13	5.82	-12.0%	5.55	6.26	-12.0%
5	0.42	0.35	18.9%	5.41	4.28	23.1%	5.84	4.63	23.1%
6	0.31	0.29	6.6%	4.43	4.08	8.1%	4.74	4.37	8.1%
7	0.11	0.10	12.0%	1.13	1.07	6.1%	1.24	1.17	5.8%
8	0.10	0.07	36.4%	0.83	0.81	6.3%	0.93	0.87	6.7%
9	0.23	0.25	-10.0%	3.71	3.60	2.4%	3.94	3.85	2.3%

6.1 Relative Accuracy

Table 6-4 displays the analytical results of the AMESA samples for individual PCDD and PCDF congeners, as well as the TEQ values for PCDDs, PCDFs and the totals determined for the AMESA samples. Note that a single composite sample was collected for Test Runs 3 and 4, as well as for Test Runs 7 and 8. As with the reference method samples, these results have been corrected to 7% O_2. In Table 6-5, the AMESA results are presented along with the averaged result from the reference method for each test run. In this table, the reference method results for Test Runs 3 and 4, and for Test Runs 7 and 8 were combined to represent a single sample totaling 16 hours. The percent difference between the reference method results and the AMESA results is shown for each test run. For all but one of the test runs, the AMESA results were lower than the reference method results. The percent differences range from 5.0% to -31.0% for all the test runs. Although the AMESA was located closer to Port 7 than to Port 1, the average of the reference method results from the two ports was used for the comparison to the AMESA.

It should be noted that the AMESA is typically used to collect long-term samples (i.e., several week duration) versus short term sampling. Therefore, this verification test does not mimic a typical real-world application of the AMESA.

It should also be noted that since the installation of the AMESA was not a standard installation because of modifications needed to accommodate the AMESA on the small duct diameter,

several potential factors which were not evaluated in this test may have contributed to bias of the AMESA relative to the reference method results. Because of the non-standard installation, it is possible that leaks occurred in the sampling train, which can result in a negative bias in analyte concentration. Also, since the nozzle could not be rinsed between runs, carry-over from run to run may have occurred.

Table 6-4. AMESA Results

Compound	Concentration [ng/dscm @ 7% O_2]						
	Test Run 1	Test Run 2	Test Run 3 - 4	Test Run 5	Test Run 6	Test Run 7 - 8	Test Run 9
2,3,7,8 - TeCDD	0.01	0.01	0.07	0.02	0.02	0.01	0.01
1,2,3,7,8 - PeCDD	0.06	0.04	0.23	0.15	0.13	0.05	0.08
1,2,3,4,7,8 - HxCDD	0.07	0.04	0.24	0.26	0.14	0.07	0.14
1,2,3,6,7,8 - HxCDD	0.08	0.05	0.28	0.30	0.17	0.08	0.17
1,2,3,7,8,9 - HxCDD	0.05	0.03	0.18	0.18	0.11	0.05	0.10
1,2,3,4,6,7,8 - HpCDD	0.72	0.23	1.36	1.23	0.97	0.61	0.72
1,2,3,4,6,7,8,9 - OCDD	1.96	0.40	2.68	2.03	1.84	1.23	1.15
2,3,7,8 - TeCDF	0.44	0.35	1.58	1.33	1.19	0.34	1.17
1,2,3,7,8 - PeCDF	0.61	0.46	2.00	1.89	1.61	0.52	1.38
2,3,4,7,8 - PeCDF	1.35	1.02	4.67	4.21	3.59	1.16	3.25
1,2,3,4,7,8 - HxCDF	1.23	0.86	4.02	3.96	3.41	1.34	2.78
1,2,3,6,7,8 - HxCDF	1.01	0.72	3.28	3.11	2.82	1.09	2.23
2,3,4,6,7,8 - HxCDF	0.94	0.49	2.97	2.67	2.53	0.99	1.94
1,2,3,7,8,9 - HxCDF	0.00	0.00	0.03	0.11	0.00	0.04	0.04
1,2,3,4,6,7,8 - HpCDF	3.45	1.65	9.57	8.76	7.52	3.41	5.74
1,2,3,4,7,8,9 - HpCDF	0.47	0.17	1.38	1.25	1.02	0.49	0.84
1,2,3,4,6,7,8,9 - OCDF	1.90	0.56	4.56	3.79	2.98	1.68	2.29
Concentration[a] [ng TEQ/dscm @ 7% O_2]							
Total PCDD TEQ	0.09	0.07	0.38	0.25	0.20	0.08	0.14
Total PCDF TEQ	1.11	0.79	3.73	3.42	2.96	1.03	2.58
Total PCDD/F TEQ	1.20	0.86	4.11	3.67	3.16	1.11	2.71

[a] TEQ values calculated using the WHO 98 TEF values.

Table 6-5. Summary of Results from the Modified Method 23 Samples and AMESA

Test Run	Average Method 23 Results (ng TEQ/dscm)	AMESA Results (ng TEQ/dscm)	Absolute Difference (ng TEQ/dscm)	Percent Difference
1	1.62	1.20	-0.42	-26.0
2	1.10	0.86	-0.24	-22.1
3 and 4[a]	5.96	4.11	-1.85	-31.0
5	5.23	3.67	-1.56	-29.8
6	4.55	3.16	-1.39	-30.6
7 and 8[a]	1.05	1.11	0.05	5.0
9	3.89	2.71	-1.18	-30.3

[a] The samples for Test Runs 3 and 4 and for Test Runs 7 and 8 were collected on a single cartridge for the AMESA and analyzed as a single 16-hour test run.

Table 6-6 shows the relative accuracy results for the AMESA, expressed as a percent as calculated by Equation (1) (Section 5.1). The RA result for combined PCDD/F measurements is 48.2%. Separately, RA calculations are 49.0% for the PCDDs and 48.2% for the PCDFs, respectively. This calculation of RA includes the absolute differences between the measurements for the test runs as well as the standard deviation of the differences for all the runs. As a result, the RA percentage results reported in Table 6-6 are greater than the percent differences shown in Table 6-5. In addition, the intermethod RSD of the differences between the AMESA and average of the Method 23 results is shown, along with the intramethod RSD between the two Method 23 trains.

Table 6-6. Relative Accuracy Results for the AMESA

Parameter	RA (%)	Intermethod RSD (%)	Intramethod RSD (%)
PCDD TEQ (n = 7)	48.2	37.4	10.0
PCDF TEQ (n = 7)	49.0	20.9	8.4
PCDD/F TEQ (n = 7)	48.2	21.9	8.4

6.2 Range

The range of the AMESA is reported in terms of percent difference from the reference method under the variety of boiler operating conditions and sampling durations used during the test runs. Overall, no clear pattern exists in terms of the percent difference as a function of total TEQ concentration. The greatest percent difference between the AMESA and Method 23 results was -31.0% and the lowest percent difference was 5.0%. The magnitude of the differences ranged from 0.05 ng TEQ/dscm to 1.85 ng TEQ/dscm.

Table 6-7 summarizes the test runs by sampling duration. The average absolute percent difference for 4-hour test runs was 27.1%, and the average absolute percent difference for the 8- and 16-hour test runs was 22.1%. Thus, there was no strong apparent dependence of AMESA accuracy relative to Method 23 on the length of the sampling run during this test.

Table 6-7. Summary of Percent Difference Values by Sampling Duration

Duration	Test Run	% Difference
16 hr	3 and 4	-31.0
16 hr	7 and 8	5.0
8 hr	9	-30.3
> 4 hr Average Absolute % Diff		22.1
4 hr	1	-26.0
4 hr	2	-22.1
4 hr	5	-29.8
4 hr	6	-30.6
4 hr Average Absolute % Diff		27.1

6.3 Data Completeness

Samples were successfully collected from each of the sampling test runs, and the results of the analyses of these samples are presented in Section 6.1. As a result, the data completeness for the AMESA was 100% for the verification test. However, as described in Section 6.4, during some of the Method 23 test runs, the AMESA did not sample the flue gas for the entire sampling period. However, overall the AMESA sampled the flue gas for approximately 97% of the total of the sampling periods (i.e., 113 minutes downtime divided by 3360 minutes test run sampling time = 3.4% downtime).

6.4 Operational Factors

Table 6-8 summarizes the activities performed on the AMESA system during the verification test, as well as the time required to perform those activities and the amount of down time experienced to complete those activities.

Table 6-8. Activity Summary for AMESA

Date	Duration	Activity	Down Time
9/12/05	20 minutes	Sample installation, instrument setup	NA[a]
9/12/05	15 minutes	Signal from O_2 CEM was not received. Operator programmed a constant O_2 concentration and started sampling	15 minutes
9/12/05	15 minutes	Sample recovery, data retrieval	NA[a]
9/13/05	15 minutes	Sample installation, instrument setup	NA[a]
9/13/05	15 minutes	Sample recovery, data retrieval	NA[a]
9/14/05	15 minutes	Sample installation, instrument setup	NA[a]
9/15/05	15 minutes	Sample recovery, data retrieval	NA[a]
9/16/05	15 minutes	Sample installation, instrument setup	NA[a]
9/16/05	50 minutes	Leak check failed, cartridge had a chip in the thread, replaced cartridge with a new one	50 minutes
9/16/05	15 minutes	Sample recovery, data retrieval	NA[a]
9/19/05	20 minutes	Sample installation, instrument setup	NA[a]
9/19/05	48 minutes	Break occurred, discovered pitot flue gas sensor tubes not connected, operator error	48 minutes
9/19/05	15 minutes	Sample recovery, data retrieval	NA[a]
9/20/05	15 minutes	Sample installation, instrument setup	NA[a]
9/21/05	15 minutes	Sample recovery, data retrieval	NA[a]
9/22/05	15 minutes	Sample installation, instrument setup	NA[a]
9/22/05	15 minutes	Sample recovery, data retrieval	NA[a]

[a] NA = Not applicable. Sample installation and recovery were performed outside of sampling period.

6.4.1 Ease of Use

The AMESA system was installed by a single representative of becker messtechnik and was completely ready for testing within 2 days after the start of installation. Operation of the AMESA system during the verification test was conducted by representatives of Battelle. During the first week of testing, the representative of Battelle who operated the AMESA system was an experienced scientist with a Ph.D. in physical chemistry and approximately 15 years of experience in operating advanced scientific equipment. During the second week of testing, the representative of Battelle who operated the AMESA system was also an experienced scientist with a bachelor's degree in chemistry and approximately five years of experience in operating advanced scientific equipment. Both representatives of Battelle were trained by a representative of becker messtechnik for a period of approximately 2 hours. During training, the representatives of Battelle were provided with a detailed overview of the basic operation of the AMESA including demonstration of several important software menus used for instrument setup and operation. Training also included a demonstration of sample installation and recovery. The

representatives of Battelle were also asked to demonstrate several hands-on activities involving sample installation/recovery, as well as system setup, to illustrate adequate training to the vendor.

Installation and retrieval of the sampling media required approximately 10 to 15 minutes for each process. However, these times were longer than would be required under normal operation since a clean probe liner and clean Teflon tubing were installed prior to each test run and removed after each test run for rinsing. During normal operation, only the sampling cartridge is installed/retrieved on a routine basis, each process requiring less than two minutes.

6.4.2 Maintenance

For the purpose of this verification report, sample installation/recovery and system setup were not considered to be maintenance activities. Outside of routine sample installation/recovery and system set-up, no maintenance was performed on the AMESA during the verification test.

6.4.3 Consumables/Waste Generation

During the verification test, the AMESA required the use of several standard consumable materials. The consumables that were used included XAD-2 resin (approximately 75 grams per sample collected) and glass wool that were used in the sampling cartridge for sample collection, as well as methylene chloride, acetone, and toluene (approximately 5 mL each) for rinsing of the sampling probe and Teflon sampling line. Note that this rinsing was needed because of the sampling configuration used in the test and would not be needed in a typical installation. Additional consumables included solvents and PCDD/F standards used in the extraction and analysis of the collected samples.

Chapter 7
Performance Summary

Table 7-1 is a summary of the results of the AMESA verification test.

Table 7-1. Summary of Verification Test Results for AMESA

Parameter Evaluated	Method of Evaluation	Results			
			PCDDs	**PCDFs**	**PCDD/Fs**
Relative accuracy	Comparison to Method 23 reference samples	RA Intermethod RSD Intramethod RSD	• 48.2% • 37.4% • 10.0%	• 49.0% • 20.9% • 8.4%	• 48.2% • 21.9% • 8.4%
Range	Percent difference comparison to Method 23 reference samples	• No dependence of accuracy on PCDD/F TEQ over range of approximately 1 to 6 ng TEQ/dscm • No dependence of accuracy on sample duration over range of 4 to 16 hours			
Data completeness	Ratio of number of samples successfully collected to number of potential samples that could have been collected	100% completeness in number of samples collected			
Ease of use	Operator observations	• Installation of the AMESA system was completed by a representative of becker messtechnik within 48 hours • Effectively operated after 2 hours of training in basic operation • Installation of sampling media and removal of sampling media completed in approximately 15 minutes each[a] • Approximately 3% down time			
Maintenance	Not applicable	No maintenance was required during the verification test.			
Consumables/waste generated	Observation	XAD-2 and glass wool were used in the sampling cartridges for sample collection. Methylene chloride, acetone, and toluene were used to rinse the probe liner and sampling tube.[a]			

[a] Installation and removal of sampling media were not typical of normal installation. The small duct diameter on the boiler required a special installation and included routine removal and rinsing of the probe liner and sampling line, which is not typically performed after each sampling period in a normal installation.

Chapter 8
References

1. U.S. EPA Method 23—*Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors*, U.S. Environmental Protection Agency, February 1991. Available at: http://www.epa.gov/ttn/emc/promgate/m-23.pdf.

2. *Test/QA Plan for Verification of Dioxin Emission Monitoring Systems (EMSs)*, Battelle, Columbus, Ohio, September 6, 2005.

3. *Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Center*, Version 5.0, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, March 2004.

4. George C. Clark, Michael Chu, Dahman Touati, Barry Rayfield, Jon Stone, and Marcus Cooke, "A Novel Low-Cost Air Sampling Device (AmbStack Sampler) and Detection System (CALUX Bioassay) for Measuring Air Emissions of Dioxin, Furan, and PCB on a TEQ Basis Tested With a Model Industrial Boiler," *Organohalogen Compounds*, **40** (1999), 79-82.