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# Environmental Technology Verification Report

MONITORING SYSTEMS GMBH  
DIOXIN MONITORING SYSTEM

Prepared by  
Battelle

**Battelle**  
*The Business of Innovation*

Under a cooperative agreement with

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

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THE ENVIRONMENTAL TECHNOLOGY VERIFICATION  
PROGRAM



## ETV Joint Verification Statement

<b>TECHNOLOGY TYPE:</b>	Dioxin Emission Monitoring System	
<b>APPLICATION:</b>	Monitoring Incinerator Emissions	
<b>TECHNOLOGY NAME:</b>	DioxinMonitoringSystem	
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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](http://www.epa.gov/etv).

ETV works in partnership with recognized standards and testing organizations, with stakeholder groups (consisting of buyers, vendor organizations, and permittees), 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 Monitoring Systems GmbH DioxinMonitoringSystem 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 DioxinMonitoringSystem 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 DioxinMonitoringSystem results to those from Method 23 reference samples collected simultaneously. Range was determined from measurements over a variety of defined operating conditions that produced differing levels of dioxins. Data completeness was assessed as the percentage of maximum data return achieved by the DioxinMonitoringSystem 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 oxygen, carbon monoxide, carbon dioxide, water, and hydrogen chloride. Reference samples were collected and analyzed for dioxins using Method 23 with several 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. Additionally, EPA QA staff conducted an independent technical systems audit.

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](http://www.epa.gov/etv/centers/center1.html).

## TECHNOLOGY DESCRIPTION

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

The DioxinMonitoringSystem is a long-term sampling device for measuring the concentrations of PCDDs in gas streams. It is an automatic isokinetic sampler for measurement of PCDDs, PCDFs, and other persistent organic pollutants. The system comprises (1) a stack-mounted dual probe system including automatic probe switching, blowback, and cleaning, with particle filter and polyurethane foam (PUF) cartridge housing attached and (2) a remote control unit for isokinetic sampling enabling automatic measurement control, remote control and data download, standby/restart, and calibration. The control unit includes both menu-driven software and a process computer. 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 a static random access memory (SRAM) card. The data on the SRAM card are later interrogated together with the analysis results to ascertain the mass concentration.

The gas is sampled isokinetically from the gas stream by alternating the use of one of two titanium probes. The collected gas is transferred to a titanium mixing chamber where it is diluted with dried and cooled air. Thus, the sampled gas is cooled by keeping the dew point below the gas mixture temperature, which avoids any condensation. The dry gas mixture then passes through a filter stack where the PCDDs are collected. The filters are designed to collect the dust fraction and the gas (or more exactly, the material passing through the filter) fraction separately. The DioxinMonitoringSystem allows most of the sampling to be conducted in an unattended fashion after an initial run configuration by the operator. This device is configured specific to the sampling location on installation, partially by the sampling institution or laboratory preparing and analyzing the cartridges and partially by the operator.

The system can also be configured as a single probe device. Both configurations can handle high dust loadings (up to 150 milligrams per cubic meter) without change in performance, and flue gas velocities up to

30 meters per second can be accommodated within the isokinetic control range of the overall system. The system can also be configured to collect samples for determining heavy metals.

**VERIFICATION RESULTS**

Parameter Evaluated	Method of Evaluation	Results			
		PCDDs	PCDFs	PCDD/Fs	
Accuracy	Comparison to Method 23 reference samples	RA	• 106%	• 18.4%	• 22.6%
		(RA) <sup>(a)</sup>	• (16.8%)	• (17.8%)	• (17.5%)
		Intermethod RSD	• 85.4%	• 10.3%	• 9.7%
		(Intermethod RSD) <sup>(b)</sup>	• (16.3%)	• (10.4%)	• (10.4%)
		Intramethod RSD	• 10.0%	• 8.4%	• 8.4%
Range	Comparison to Method 23 reference samples by concentration and sample collection time	<ul style="list-style-type: none"> <li>No dependence of accuracy on PCDD/F toxic equivalent (TEQ) over range of approximately 1 to 6 nanograms TEQ/dry standard cubic meter</li> <li>No dependence of accuracy on sample duration over range of 4 to 16 hours.</li> </ul>			
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	<ul style="list-style-type: none"> <li>Installation of the DioxinMonitoringSystem was completed by a representative of MonitoringSystems, GmbH, within 48 hours</li> <li>Effectively operated after 1-2 hours of training in basic operation</li> <li>Installation of sampling media and removal of sampling media completed in approximately 5-15 minutes each</li> <li>Less than 1% downtime</li> </ul>			
Maintenance	Operator observations	No maintenance was required during the verification test.			
Consumables/waste generated	Operator observations	PUF cartridges were used in the sampling cartridges for sample collection.			

<sup>(a)</sup> RA calculated using only congeners detected in both the DioxinMonitoringSystem and Method 23 samples.

<sup>(b)</sup> Intermethod relative standard deviation (RSD) calculated using only congeners detected in both the DioxinMonitoringSystem and Method 23 samples.

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June 2006

# Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

MonitoringSystems GmbH  
DioxinMonitoringSystem

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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 permittees, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of six 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>.



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- Chlorine Chemistry Council
- U.S. EPA Office of Solid Waste and Emergency Response
- U.S. EPA Office of Air Quality Planning and Standards
- U.S. EPA Office of Research and Development.

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## List of Abbreviations

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
NIST	National Institute of Standards and Technology
PCDD	polychlorinated dibenzo-p-dioxins
PCDF	polychlorinated dibenzofurans
PE	performance evaluation
PUF	polyurethane foam
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



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## 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.

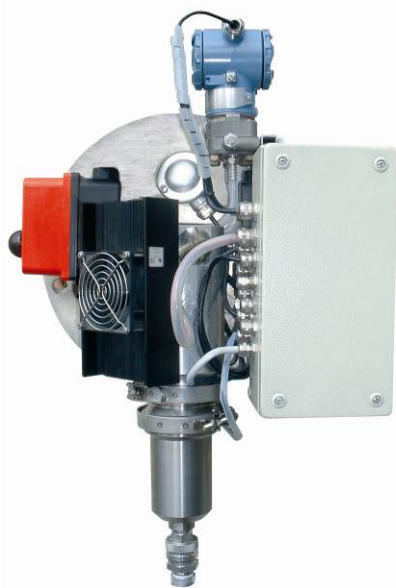
ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permittees; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test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

The EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of the MonitoringSystems, GmbH, DioxinMonitoringSystem 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 DioxinMonitoringSystem. Following is a description of the DioxinMonitoringSystem, based on information provided by the vendor. The information provided below was not verified in this test.

The DioxinMonitoringSystem is a long-term sampling device for measuring the concentrations of PCDDs in gas streams. It is an automatic isokinetic sampler for measurement of PCDDs, PCDFs, and other persistent organic pollutants.



**Figure 2-1 Photograph of DioxinMonitoringSystem Probe System**

The system comprises:

- A stack mounted dual probe system including automatic probe switching, blowback and cleaning, with particle filter and polyurethane foam (PUF) cartridge housing attached (shown in Figure 2-1).
- A remote control unit for isokinetic sampling enabling automatic measurement control, remote control and data download, standby/restart, and calibration. Measurement data for each sample cartridge can be accessed after the sampling period.

The control unit includes both menu-driven software and a process computer. The system is operated by five keys and a liquid crystal display screen. This screen is also used to set parameters and retrieve important operational data. All data relevant for measurements are stored in the form of parameters that 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 a static random access memory (SRAM) card. The data on the SRAM card are later interrogated together with the analysis results to ascertain the mass concentration.

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The gas is sampled isokinetically from the gas stream by alternating the use of one of two titanium probes. The collected gas is transferred to a titanium mixing chamber where it is diluted with dried and cooled air. Thus, the sampled gas is cooled by keeping the dew point below the gas mixture temperature, which avoids any condensation. The dry gas mixture then passes through a filter stack where the PCDDs are collected. The filters are designed to collect the dust fraction and the gas (or more exactly, the material passing through the filter) fraction separately. The collected samples are then retrieved and sent to a laboratory for analysis. The time required for sample analysis will vary depending on the method employed and the laboratory response time. Typical turnaround times for PCDD/F analysis are between two and four weeks. For this verification test, the collected gas samples were analyzed in the same laboratory and by the same method as the reference samples collected during the test.

The DioxinMonitoringSystem allows most of the sampling to be conducted in an unattended fashion after an initial run configuration by the operator. This device configuration is done specific to the sampling location on installation, partially by the sampling institution or laboratory preparing and analyzing the cartridges and partially by the operator.

The system can also be configured as a single probe device. Both configurations can handle high dust loadings (up to 150 milligrams per cubic meter) without change in performance, and flue gas velocities up to 30 meters per second can be accommodated within the isokinetic control range of the overall system. The system can also be configured to collect samples for determining heavy metals.

The system can be controlled and periodically checked using a local area network interface or remote access via the internet. Data can be downloaded through these links, and remote services can be implemented.



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## Chapter 3 Test Design and Procedures

### 3.1 Introduction

EPA Method 23<sup>(1)</sup> is the certified extractive method used for quantifying dioxin 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 dioxins and may have the potential to provide more information on dioxin 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 DioxinMonitoringSystem 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 DioxinMonitoringSystem were determined through comparisons to a modified version of Method 23 integrated sampling method for PCDD/PCDFs, with modifications as described in Section 3.2.2 of this report.<sup>(1)</sup> 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)*,<sup>(2)</sup> and the *Quality Management Plan (QMP) for the ETV/AMS Center*.<sup>(3)</sup> As described in this report, the performance of the DioxinMonitoringSystem 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 DioxinMonitoringSystem 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 PCDDs. Data completeness was assessed as the percentage of maximum data return achieved by the DioxinMonitoringSystem 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



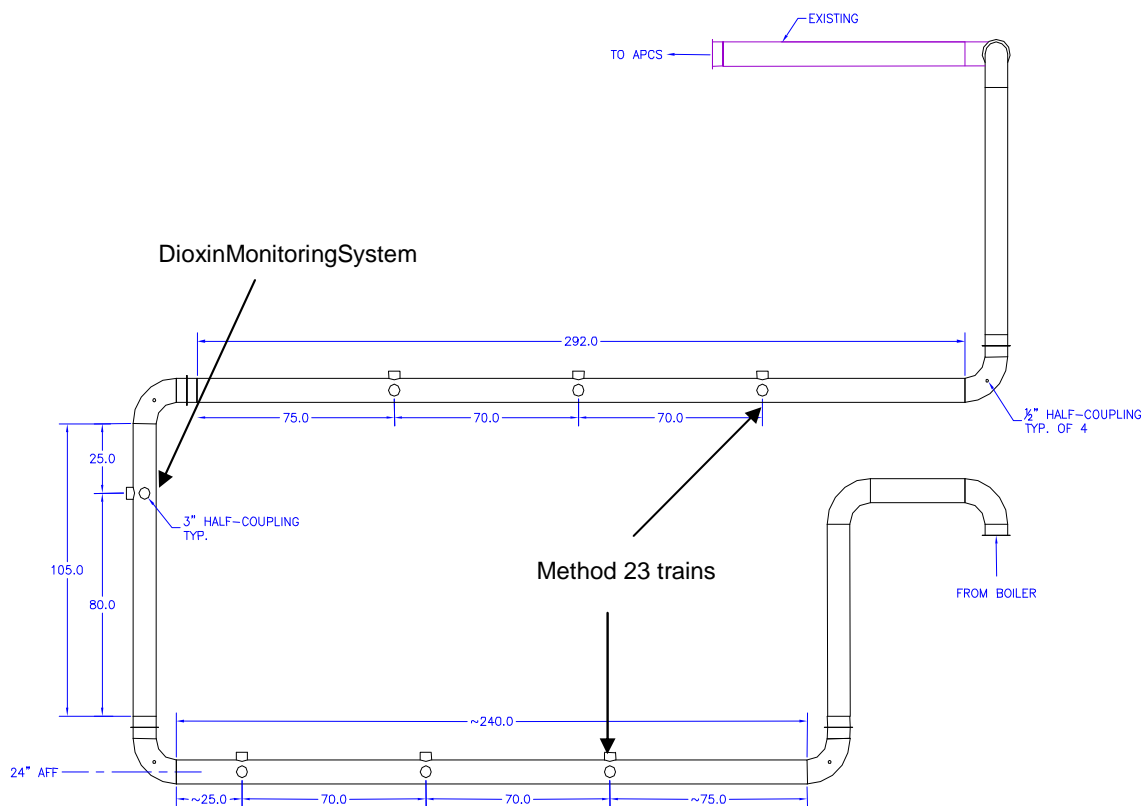
**Figure 3-1. Wetback Scotch Marine Package Boiler**

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 oxygen ( $O_2$ ) and carbon dioxide ( $CO_2$ ) emission concentrations.

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 dioxin EMSs and operation of duplicate Method 23 sampling trains. Figure 3-2 shows a schematic illustration of the duct, identifying the sampling locations for the reference sample trains and the DioxinMonitoringSystem. As this figure shows, one Method 23 train sampled from a port upstream in the flue gas flow from the DioxinMonitoringSystem's sampling port, and the other sampled downstream.



**Figure 3-2. Illustration of Flue Gas Duct with Sampling Locations**

A surrogate chlorinated chemical (1,2-dichlorobenzene) and a source of metal atoms (copper naphthenate) were added to the boiler fuel to promote dioxin formation for the EMS testing.<sup>(4)</sup> A surrogate feed system was designed to safely tap the surrogate 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 surrogate 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 dioxins using Method 23, with the following modifications established before any sample collection took place:

- 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, surrogate, and recovery 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 dioxins and furans (see Section 4.1.2).

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 Dioxin Monitoring System 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.

#### *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 collected in a single 250-milliliter (mL) amber jar. The probe and front-half filter housing were then rinsed with toluene and 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 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 DioxinMonitoringSystem Installation and Operation

Figure 3-3 shows the DioxinMonitoringSystem sampling unit on the duct. Immediately prior to each test run, a PUF sampling cartridge was installed in the DioxinMonitoringSystem sampling unit. During the verification test, the DioxinMonitoringSystem was



**Figure 3-3. Installed DioxinMonitoringSystem Sampling Probe**

manually started and programmed to stop automatically after completion of each test run. The DioxinMonitoringSystem can also be programmed for automated start-up to allow for unattended operation. After completion of each test run, the sampling cartridge was removed and stored in a freezer until transport to the laboratory for analysis. Sampling data for each test run were downloaded, printed out, and supplied to the laboratory for use in determining PCDD/F concentrations.

which was located approximately 2 meters from the sampling unit.

Figure 3-4 shows the control unit of the DioxinMonitoringSystem system





**Figure 3-4. Dioxin Monitoring System Control Unit**

### 3.3 Test Design

RA, range, data completeness, and operational factors for the Dioxin Monitoring System were evaluated.

#### 3.3.1 Relative Accuracy

The RA of the Dioxin Monitoring System 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 Dioxin Monitoring System was installed, as shown in Figure 3-2. The reference samples were recovered and submitted for analysis by the modified version of Method 23 described in Section 3.2. The PCDD/F concentrations determined by the reference methods were compared to corresponding results from the

Dioxin Monitoring System, 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 Dioxin Monitoring System was evaluated. Two sets of operating conditions were used for the test runs to generate expected high (5-10 ng TEQ/dscm) and low (1-2 ng TEQ/dscm) PCDD/F 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 toxic equivalents per dry standard cubic meter (TEQ/dscm), corrected to 7% O<sub>2</sub>. 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

**Table 3-1. Test Run Summary**

Date	Test Run	Sampling Duration	Expected PCDD/F Concentration <sup>(a)</sup>
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

<sup>(a)</sup> 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.

reference data used for comparison to the DioxinMonitoringSystem results. If discrepancies of greater than 30% were observed, the data were flagged and the samples treated as independent samples for comparison to the DioxinMonitoringSystem.

**3.3.2 Range**

Range was assessed in terms of RA over the range of measured PCDD/F 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 DioxinMonitoringSystem 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 DioxinMonitoringSystem. It was reported in terms of the percentage of acceptable samples collected during the verification test and in terms of percentage of time that the DioxinMonitoringSystem system was collecting samples compared with the Method 23 sampling trains.

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#### 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.



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## Chapter 4

### Quality Assurance/Quality Control

QA/QC procedures were performed in accordance with the QMP for the AMS Center<sup>(3)</sup> and the test/QA plan<sup>(2)</sup> 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/F 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**

<b>Critical Measurement</b>	<b>PE Audit Method</b>	<b>Acceptance Criteria</b>	<b>Audit Results</b>
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/F internal standard recovery	Method spike with an independent PCDD/F standard	40 to 130% for tetra-through hexachlorinated compounds; and 25 to 130% for hepta- and octachlorinated compounds	101 – 120% Pass
PCDD/F surrogate standard recovery	Field spike with an independent PCDD/F 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 dioxin 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,<sup>(3)</sup> the test/QA plan,<sup>(2)</sup> 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 of 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.

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### **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.<sup>(3)</sup> 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 DioxinMonitoringSystem during this verification test.

### 5.1 Relative Accuracy

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

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

where:

- $|\bar{d}|$  = the absolute value of the mean of the differences between the DioxinMonitoringSystem 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 DioxinMonitoringSystem 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):

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

where

- 
- $SD_i$  = the standard deviation of the paired DioxinMonitoringSystem and reference method results for test run  $i$ ,
- $X_i$  = the average of the paired DioxinMonitoringSystem 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 DioxinMonitoringSystem 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 Dioxin Monitoring System 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. (°F)	O <sub>2</sub> Conc. (%)	CO <sub>2</sub> Conc. (%)	H <sub>2</sub> O Conc. (%)
1	9/12/2005	4	Low	312.0	4.28	12.85	11.0
2	9/13/2005	4	Low	313.5	4.72	12.77	10.8
3	9/14/2005 <sup>(a)</sup>	8	High	305.5	4.30	12.98	11.1
4	9/15/2005 <sup>(a)</sup>	8	High	309.5	5.38	12.22	11.0
5	9/16/2005	4	High	319.0	5.04	12.31	11.0
6	9/19/2005	4	High	316.5	5.09	12.23	10.8
7	9/20/2005 <sup>(a)</sup>	8	Low	303.0	4.8	12.36	11.9
8	9/21/2005 <sup>(a)</sup>	8	Low	305.5	3.12	13.35	11.7
9	9/22/2005	8	High	315.5	3.38	13.04	11.1

<sup>(a)</sup> The samples for Test Runs 3 and 4 and 7 and 8 were collected on a single cartridge for the Dioxin Monitoring System 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 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 dioxin and furan congeners. The lower portion of the table summarizes the TEQ values for each test run according to PCDDs, PCDFs, and the total. All results were corrected to 7% O<sub>2</sub>.

**Table 6-2. Reference Method 23 Results**

Compound	Concentration [ng/dscm @ 7% O <sub>2</sub> ]																	
	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
Total PCDD TEQ	Concentration [ng TEQ /dscm @ 7% O <sub>2</sub> ]																	
	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
<b>Total PCDD TEQ</b>	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
<b>Total PCDF TEQ</b>	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
<b>Total PCDD/F TEQ</b>	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

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 PCDDs in Test Run 8, the results from the two trains are all 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 is magnified because of the low absolute concentrations of PCDDs in that run. 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, the average of the results was used in all cases for evaluation of the DioxinMonitoringSystem.

**Table 6-3. Results from the 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 DioxinMonitoringSystem samples for individual dioxin and furan congeners, as well as the TEQ values for PCDDs, PCDFs and the PCDD/F totals. 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<sub>2</sub>. In Table 6-5, the DioxinMonitoringSystem 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 also for Test Runs 7 and 8 were each combined to represent a single sample totaling 16 hours. The percent difference between the reference method results and the DioxinMonitoringSystem results is shown for each test run. For all but one test run, the DioxinMonitoringSystem results were lower than the reference method results. The percent differences range from -18.7% to 18.0% for all the test runs.



**Table 6-4. Dioxin Monitoring System Results**

Compound	Concentration [ng/dscm @ 7% O <sub>2</sub> ]						
	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	ND	ND	ND	ND	ND	ND	ND
1,2,3,7,8 - PeCDD	ND	ND	0.25	ND	ND	0.06	0.13
1,2,3,4,7,8 - HxCDD	ND	ND	0.21	ND	0.23	0.05	0.16
1,2,3,6,7,8 - HxCDD	ND	ND	ND	ND	0.30	ND	0.28
1,2,3,7,8,9 - HxCDD	ND	ND	0.20	ND	ND	0.04	0.12
1,2,3,4,6,7,8 - HpCDD	0.86	0.42	1.55	1.55	1.13	0.34	0.95
1,2,3,4,6,7,8,9 - OCDD	1.96	0.94	2.77	2.72	2.08	0.58	1.53
2,3,7,8 - TeCDF	0.84	0.42	2.11	1.39	1.28	0.30	1.37
1,2,3,7,8 - PeCDF	1.04	0.54	3.08	2.42	1.96	0.52	1.85
2,3,4,7,8 - PeCDF	2.57	1.27	6.05	5.28	4.42	1.11	4.15
1,2,3,4,7,8 - HxCDF	1.77	1.15	6.21	5.40	4.58	1.45	4.29
1,2,3,6,7,8 - HxCDF	1.36	0.86	6.10	4.09	3.51	1.09	3.21
2,3,4,6,7,8 - HxCDF	1.22	0.75	3.12	2.81	2.56	0.73	2.21
1,2,3,7,8,9 - HxCDF	ND	ND	0.26	0.27	0.18	0.06	0.19
1,2,3,4,6,7,8 - HpCDF	4.05	2.34	12.66	12.82	10.51	3.07	8.78
1,2,3,4,7,8,9 - HpCDF	0.92	0.46	1.76	1.64	1.18	0.32	1.21
1,2,3,4,6,7,8,9 - OCDF	2.00	1.22	5.71	5.08	3.31	0.89	3.13
Concentration [ng TEQ/dscm @ 7% O <sub>2</sub> ]							
<b>Total PCDD TEQ</b>	0.01	0.00	0.31	0.02	0.06	0.08	0.20
<b>Total PCDF TEQ</b>	1.91	1.01	5.10	4.30	3.64	0.98	3.39
<b>Total PCDD/F TEQ</b>	1.92	1.01	5.41	4.32	3.70	1.06	3.59

ND – Not detected

**Table 6-5. Summary of Results from the Method 23 Reference Samples and DioxinMonitoringSystem**

Test Run	Average Method 23 Total PCDD/F Results (ng TEQ/dscm)	DioxinMonitoringSystem Total PCDD/F Results (ng TEQ/dscm)	Difference (ng TEQ/dscm)	Percent Difference
1	1.62	1.92	0.29	18.0
2	1.10	1.01	-0.09	-8.3
3 and 4 <sup>(a)</sup>	5.96	5.41	-0.54	-9.1
5	5.23	4.32	-0.91	-17.5
6	4.55	3.70	-0.85	-18.7
7 and 8 <sup>(a)</sup>	1.05	1.06	0.00	0.3
9	3.89	3.59	-0.30	-7.7

<sup>(a)</sup> The samples for Test Runs 3 and 4 and 7 and 8 were collected on a single cartridge for the DioxinMonitoringSystem and analyzed as a single 16-hour test run.

Table 6-6 shows the relative accuracy results for the DioxinMonitoringSystem, expressed as a percent as calculated by Equation (1) (Section 5.1). The RA result for combined PCDD/F measurements is 22.6%. Separately, RA calculations are 106.0% for the PCDDs and 18.4% for the PCDFs. None of the PCDD results were above 0.5 ng TEQ/dscm, so the RA% is large (106.0%) although the magnitude of the differences between the reference method and the DioxinMonitoringSystem are small, such that it has little impact on the total PCDD/F RA%. 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. Furthermore, as seen in Table 6-4, in several instances there were congeners that were not detected in the analysis of the DioxinMonitoringSystem samples. The DioxinMonitoringSystem is typically used to collect samples over periods of weeks rather than hours, so it is not unexpected that some congeners were not detected in the collected samples. To remove the influence of non-detects, the RA was also calculated using only those congeners that were detected in both the DioxinMonitoringSystem and the Method 23 samples. These values are included parenthetically in Table 6-6. In addition, the intermethod RSD of the differences between the DioxinMonitoringSystem and average of the Method 23 results is shown along with the intramethod RSD between the two Method 23 trains. The intermethod RSD calculated excluding non-detected congeners is presented parenthetically.

**Table 6-6. Relative Accuracy Results for the Dioxin Monitoring System**

Parameter	RA (%)	Intermethod RSD (%)	Intramethod RSD (%)
PCDD TEQ (n = 7)	106.0 (16.8%) <sup>(a)</sup>	85.4 (16.3%) <sup>(b)</sup>	10.0
PCDF TEQ (n = 7)	18.4 (17.8%) <sup>(a)</sup>	10.3 (10.4%) <sup>(b)</sup>	8.4
PCDD/F TEQ (n = 7)	22.6 (17.5%) <sup>(a)</sup>	9.7 (10.4%) <sup>(b)</sup>	8.4

<sup>(a)</sup> – RA calculated using only congeners detected in both the Dioxin Monitoring System and Method 23 samples.

<sup>(b)</sup> – Intermethod RSD calculated using only congeners detected in both the Dioxin Monitoring System and Method 23 samples.

## 6.2 Range

The range of the Dioxin Monitoring System 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. Table 6-5 shows that, overall, no clear pattern exists in terms of the percent difference as a function of total TEQ concentration. The greatest absolute percent difference between the Dioxin Monitoring System and Method 23 results was 18.7%, and the smallest absolute percent difference was 0.3%.

Table 6-7 summarizes the test runs by sampling duration. The average of the absolute values of the individual percent differences for 4-hour test runs was 15.6%, and the average for the 8- and 16-hour test runs was 5.7%. The percent differences varied considerably within both groups. For example, the largest positive difference (18.0%) and the largest negative difference (-18.7%) both occurred in the set of 4-hour samples. There was no apparent dependence of Dioxin Monitoring System accuracy relative to Method 23 on the length of the sampling run during this test, since the observed differences were on the same order of magnitude as the differences between the duplicate Method 23 trains.

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

Duration	Test Run	% Difference
16 hr	3 and 4	-9.1
16 hr	7 and 8	0.3
8 hr	9	-7.7
> 4 hr Average Absolute % Diff		5.7
4 hr	1	18.0
4 hr	2	-8.3
4 hr	5	-17.5
4 hr	6	-18.7
4 hr Average Absolute % Diff		15.6

### 6.3 Data Completeness

Samples were successfully collected from all 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 DioxinMonitoringSystem was 100% for the verification test.

### 6.4 Operational Factors

Table 6-8 summarizes the activities performed on the DioxinMonitoringSystem 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 DioxinMonitoringSystem**

Date	Duration	Activity	Down Time
9/12/05	15 minutes	Sample installation, instrument set-up, diagnostics	NA <sup>a</sup>
9/12/05	5 minutes	Sample recovery, data retrieval	NA <sup>a</sup>
9/13/05	15 minutes	Sample installation, instrument set-up, diagnostics	NA <sup>a</sup>
9/13/05	5 minutes	Sample recovery, data retrieval	NA <sup>a</sup>
9/14/05	15 minutes	Sample installation, instrument set-up, diagnostics	NA <sup>a</sup>
9/15/05	5 minutes	Sample recovery, data retrieval	NA <sup>a</sup>
9/16/05	15 minutes	Sample installation, instrument set-up, diagnostics	NA <sup>a</sup>
9/16/05	5 minutes	Sample recovery, data retrieval	NA <sup>a</sup>
9/19/05	15 minutes	Sample installation, instrument set-up, diagnostics	NA <sup>a</sup>
9/19/05	5 minutes	Sample recovery, data retrieval	NA <sup>a</sup>
9/20/05	15 minutes	Sample installation, instrument set-up, diagnostics	NA <sup>a</sup>
9/20/05	10 minutes	Failed leak test, inspected inner filter and removed excess filter from seal	10
9/21/05	5 minutes	Sample recovery data retrieval	NA <sup>a</sup>
9/22/05	15 minutes	Sample installation, instrument set-up, diagnostics	NA <sup>a</sup>
9/22/05	5 minutes	Sample recovery data retrieval	NA <sup>a</sup>

<sup>(a)</sup> NA = Not applicable. Sample installation and recovery are performed outside of sampling period.

#### 6.4.1 Ease of Use

The DioxinMonitoringSystem was installed by a single representative of MonitoringSystems, GmbH and was completely ready for testing within 2 days after the start of installation. Operation of the DioxinMonitoringSystem during the verification test was conducted by a representative of MonitoringSystems, GmbH. Instruction was given to representatives of Battelle

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for approximately one hour on operation of the DioxinMonitoringSystem, including installation and retrieval of sampling media, and programming of the system for automated sample collection. This instruction was sufficient for basic operation of the DioxinMonitoringSystem. More thorough instruction would be necessary for more advanced activities associated with the system.

Installation and retrieval of the sampling media required approximately 5 to 15 minutes for each process. The DioxinMonitoringSystem experienced approximately 10 minutes of downtime during the verification test which accounts for <1% of the total sampling time for all test runs combined.

#### ***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 setup, no maintenance was performed on the DioxinMonitoringSystem during the verification test.

#### ***6.4.3 Consumables/Waste Generation***

During the verification test, the DioxinMonitoringSystem required the use of several standard consumable materials. The consumables that were used included PUF cartridges that were used in the sampling cartridge for sample collection. Additional consumables included solvents and dioxin standards used in the extraction and analysis of the collected samples.

## Chapter 7 Performance Summary

Table 7-1 presents a summary of the results of the verification of the Dioxin Monitoring System system during this verification test.

**Table 7-1. Summary of Verification Test Results for Dioxin Monitoring System**

Parameter Evaluated	Method of Evaluation	Results			
			PCDDs	PCDFs	PCDD/Fs
Accuracy	Comparison to Method 23 reference samples	RA	• 106%	• 18.4%	• 22.6%
		(RA) <sup>(a)</sup>	• (16.8%)	• (17.8%)	• (17.5%)
		Intermethod RSD	• 85.4%	• 10.3%	• 9.7%
		(Intermethod RSD) <sup>(b)</sup>	• (16.3%)	• (10.4%)	• (10.4%)
		Intramethod RSD	• 10.0%	• 8.4%	• 8.4%
Range	Comparison to Method 23 reference samples by concentration and sample collection time	<ul style="list-style-type: none"> <li>• No dependence of accuracy on PCDD/F TEQ over range of approximately 1 to 6 ng TEQ/dscm</li> <li>• No dependence of accuracy on sample duration over range of 4 to 16 hours.</li> </ul>			
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	<ul style="list-style-type: none"> <li>• Installation of the Dioxin Monitoring System was completed by a representative of Monitoring Systems, GmbH, within 48 hours</li> <li>• Effectively operated after 1-2 hours of training in basic operation</li> <li>• Installation of sampling media and removal of sampling media completed in approximately 5-15 minutes each</li> <li>• Less than 1% downtime</li> </ul>			
Maintenance	Operator observations	No maintenance was required during the verification test.			
Consumables/waste generated	Operator observations	PUF cartridges were used in the sampling cartridges for sample collection.			

<sup>(a)</sup> – RA calculated using only congeners detected in both the Dioxin Monitoring System and Method 23 samples.

<sup>(b)</sup> – Intermethod RSD calculated using only congeners detected in both the Dioxin Monitoring System and Method 23 samples.

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## Chapter 8 References

1. U.S. EPA Method 23—*Determination of Polychlorinated Dibenzop-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),