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June 2006

Environmental Technology Verification Report

SRI INTERNATIONAL
JET-REMPI
(RESONANCE ENHANCED MULTI-
PHOTON IONIZATION)

Prepared by
Battelle

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The Business of Innovation

Under a cooperative agreement with

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

US EPA ARCHIVE DOCUMENT

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THE ENVIRONMENTAL TECHNOLOGY VERIFICATION
PROGRAM



ETV Joint Verification Statement

TECHNOLOGY TYPE: Dioxin Emission Monitoring System

APPLICATION: Monitoring Incinerator Emissions

**TECHNOLOGY
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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 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 SRI Jet-REMPI (resonance enhanced multi-photon ionization) 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 Jet-REMPI 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 Jet-REMPI 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 Jet-REMPI 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 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 Jet-REMPI is based on information provided by the vendor. This technology description was not verified in this test.

Jet-REMPI is an analytical technique that is designed to selectively identify and quantify vapor-phase constituents present at part-per-trillion levels in incinerator emissions without preconcentration or sample collection. Ions produced by REMPI are typically detected using a time-of-flight mass spectrometer (TOF-MS) that takes advantage of the pulsed nature and well-defined temporal character of laser ionization. Simultaneous detection by mass and wavelength yields the extremely high chemical selectivity crucial to identifying one trace compound in the midst of many other similar ones.

The laser system used in the verification test consists of a Nd:YAG pumped OPOTEK Vibrant OPO with frequency doubling unit with a nominal tuning range between 250 and 340 nanometers, a 5-nanosecond pulse width, and a repetition rate of 10 hertz. The optical line width of the system is approximately 2 centimeters (cm^{-1}). The pulsed valve is an unmodified General Valve Series 9 unit, with an orifice diameter of 0.5 millimeter. The nominal opening time was 150 microseconds, with a 2.5-cm separation between the exit of the valve and the ionization region. With the sample reservoir at atmospheric pressure, the two 250-liters-per-second turbomolecular pumps (Varian Turbo V-250) maintain pressures in the ionization chamber and mass spectrometer regions of 10^{-5} Torr, and 5×10^{-7} Torr, respectively. The mass spectrometric capabilities of the reflectron-type TOF mass analyzer used in this verification test include an upper mass range typically up to 500 atomic mass units and mass resolution ($m/\Delta m$) greater than 500.

VERIFICATION RESULTS

| Parameter Evaluated | Method of Evaluation | Results | |
|-----------------------------|---|---|---|
| | | Relative accuracy | Comparison to Method 23 reference samples |
| | | Intermethod RSD | 61.5% |
| | | Intramethod RSD | 8.4% |
| Range | Comparison to Method 23 reference samples | <ul style="list-style-type: none"> • Apparent dependence of accuracy on PCDD/F toxic equivalent (TEQ) over range of approximately 1 to 6 nanograms TEQ/dry standard cubic meters with better agreement at high concentration • Apparent dependence of accuracy on sample duration over range of 4 to 8 hours with better agreement for longer sampling duration | |
| Data completeness | Ratio of number of samples successfully collected to number of potential samples that could have been collected | <ul style="list-style-type: none"> • 100% completeness in number of samples collected • Approximately 7% downtime | |
| Ease of use | Operator observations | <ul style="list-style-type: none"> • Time required for installation of the Jet-REMPI system was not verified • Significant on-site support was needed during testing. During routine operation, a representative of ARCADIS was on-site and constantly monitoring instrument diagnostic and indicator signal • Extensive training and experience with advanced knowledge of mass spectrometry and laser spectroscopy techniques is required for operation of the Jet-REMPI and interpretation of the results | |
| Maintenance | Verification test staff observations | Repair of a faulty pulsed valve on a parallel Jet-REMPI unit was required during the verification test. The maintenance activities resulted in approximately 4 hours of instrument downtime. | |
| Consumables/waste generated | | Small amounts of compressed gas and calibration gas standards were used during the verification test. | |

RSD = relative standard deviation

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June 2006

Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

SRI International
JET-REMPI
(RESONANCE ENHANCED MULTI-
PHOTON IONIZATION)

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Notice

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development, has financially supported the development of the technology evaluated in this verification test. 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 technology centers. Information about each of these centers can be found on the Internet at <http://www.epa.gov/etv/>.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. 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 |
| cm | centimeter |
| dscm | dry standard cubic meter |
| EMS | emission monitoring system |
| EPA | U.S. Environmental Protection Agency |
| ETV | Environmental Technology Verification |
| HW | hot/wet |
| m ³ | cubic meter |
| mL | milliliter |
| ng | nanogram |
| NIST | National Institute of Standards and Technology |
| nm | nanometer |
| PCDD | polychlorinated dibenzo-p-dioxins |
| PCDF | polychlorinated dibenzofurans |
| PE | performance evaluation |
| QA | quality assurance |
| QC | quality control |
| QMP | quality management plan |
| RA | relative accuracy |
| REMPI | resonance enhanced multiphoton ionization |
| RSD | relative standard deviation |
| RTP | Research Triangle Park |
| SMPB | Scotch Marine Packaged Boiler |
| TEQ | toxic equivalent |
| TOF | time of flight |
| 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 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 SRI International Jet-REMPI (resonance enhanced multi-photon ionization) system for 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 Jet-REMPI. Following is a description of the Jet-REMPI, based on information provided by the vendor. The information provided below was not verified in this test.

Jet-REMPI (Figure 2-1) is an analytical technique that is designed to selectively identify and quantify vapor-phase constituents present at part-per-trillion levels in incinerator emissions

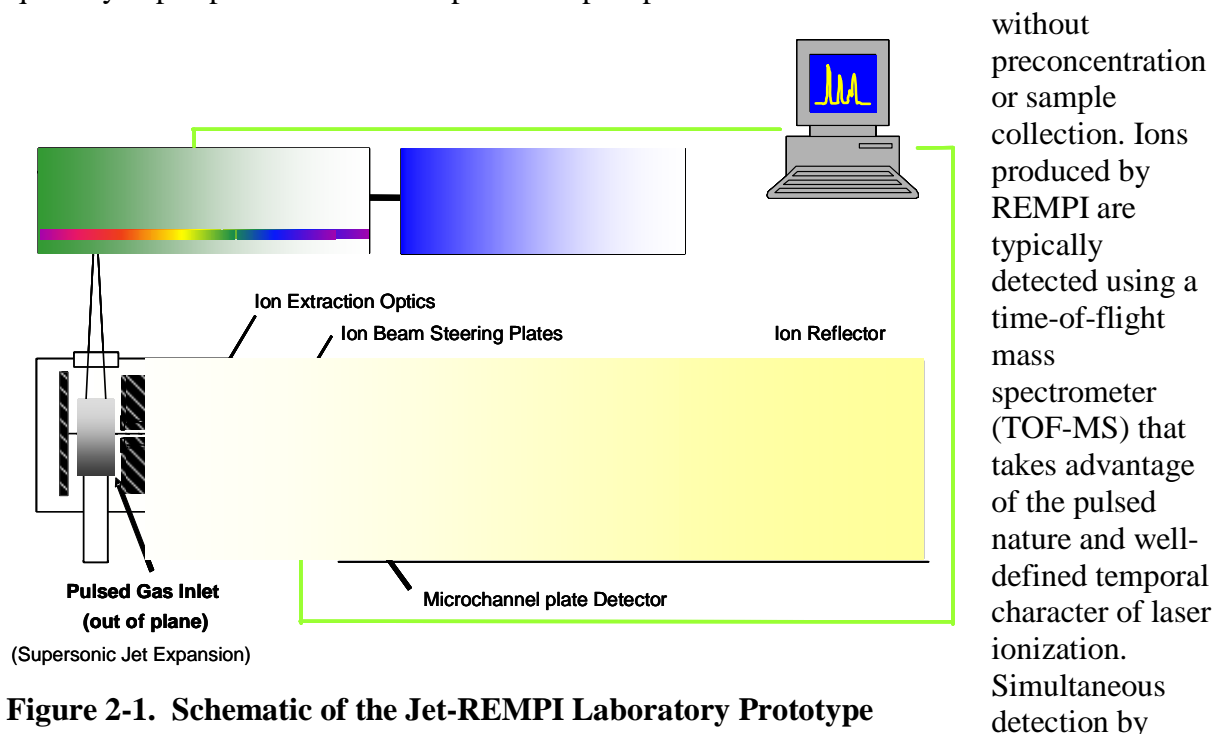


Figure 2-1. Schematic of the Jet-REMPI Laboratory Prototype

mass and wavelength yields the extremely high chemical selectivity crucial to identifying one trace compound in the midst of many other similar ones.

The laser system used in the verification test consists of a Nd:YAG pumped OPOTEK Vibrant OPO with frequency doubling unit with a nominal tuning range between 250 and 340 nanometers, a 5-nanosecond pulse width, and a repetition rate of 10 hertz. The optical line

width of the system is approximately 2 centimeters (cm)⁻¹. The pulsed valve is an unmodified General Valve Series 9 unit, with an orifice diameter of 0.5 millimeter. The nominal opening time was 150 microseconds, with a 2.5-cm separation between the exit of the valve and the ionization region. With the sample reservoir at atmospheric pressure, the two 250-liters-per-second turbomolecular pumps (Varian Turbo V-250) maintain pressures in the ionization chamber and mass spectrometer regions of 10⁻⁵ Torr, and 5 x 10⁻⁷ Torr, respectively. The mass spectrometric capabilities of the reflectron-type TOF mass analyzer used in this verification test include an upper mass range typically up to 500 atomic mass units and mass resolution (m/Δm) greater than 500.

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 Jet-REMPI 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 Jet-REMPI were determined through comparisons to a modified version of Method 23 integrated sampling method for PCDD/PCDF,⁽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 Jet-REMPI was evaluated in terms of

- Relative accuracy (RA),
- Range,

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

Relative accuracy and range were determined by comparing Jet-REMPI results to those from Method 23 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 Jet-REMPI 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

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 were 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 (Bodensewerk), 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 Jet-REMPI. As this figure shows, one Method 23 train sampled from a port upstream in the flue gas flow from the Jet-REMPI's sampling port, and the other sampled downstream.

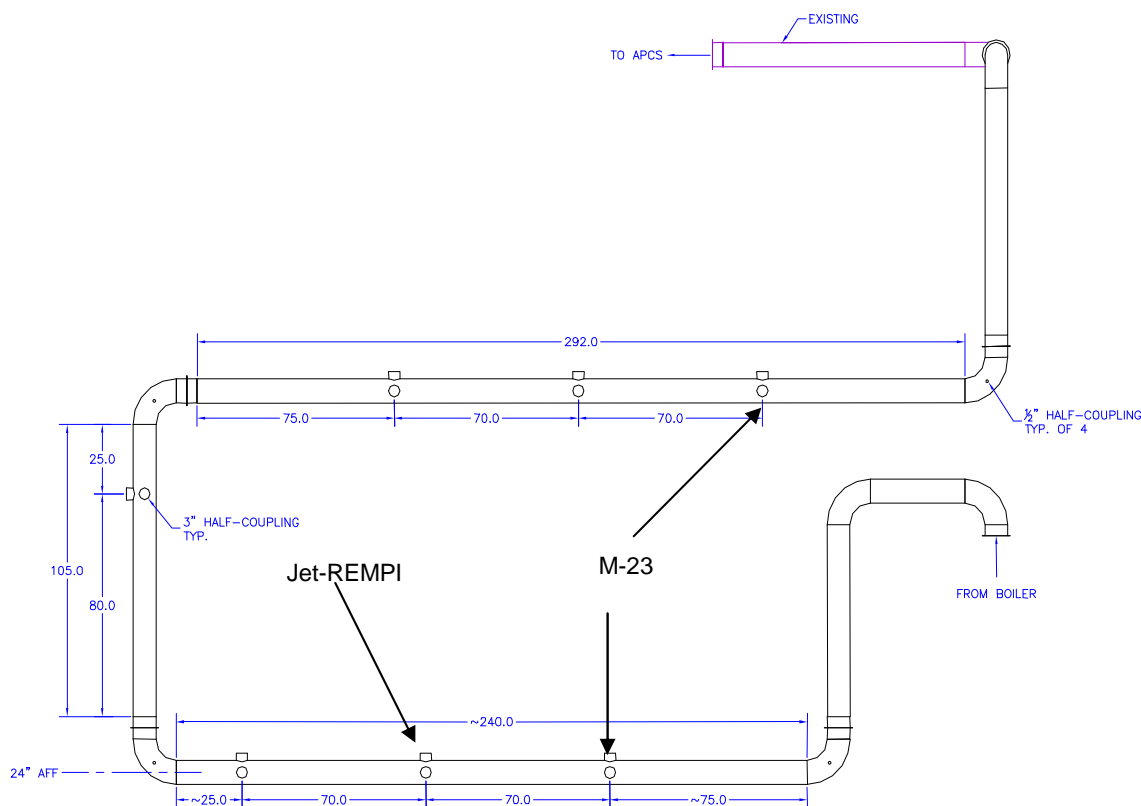


Figure 3-2. Illustration of Flue Gas Duct with Sampling Locations

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 chemical 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.

The stack gas composition for each test run conducted during the verification test is 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:

-
- 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 PCDD/PCDF (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. 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 Method 23 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 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 trains, 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 Jet-REMPI Installation and Operation

Figure 3-2 indicates the locations of the Method 23 reference sampling ports and the location of the Jet-REMPI sampling port. The flue gas was exhausted through an insulated duct with an internal diameter of approximately 20 centimeters. The duct was modified prior to testing to accommodate the installation and simultaneous operation of multiple EMS technologies in addition to sampling ports for collecting Method 23 reference samples.

During testing, a sampling probe was used to draw sample gas from the duct into a heated sample line approximately 10 meters in length that was used to deliver the flue gas from the duct to the Jet-REMPI. PCDD/F surrogate compounds were continuously monitored by Jet-REMPI.

3.3 Test Design

Relative accuracy, range, data completeness, and operational factors for the Jet-REMPI were evaluated.

3.3.1 Relative Accuracy

The RA of the Jet-REMPI 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 Jet-REMPI 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/PCDF concentrations determined by the reference methods were compared to corresponding results from the Jet-REMPI, 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 Jet-REMPI was evaluated. Two sets of operating conditions were used for the test runs to generate expected high (5-10 nanograms [ng] toxic equivalent [TEQ]/dry standard cubic meter [dscm]) and low (1-2 ng TEQ/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 samples collected over 8-hour sampling periods. 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.

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 | 3 | 8 hours | High |
| 9/15/05 | 4 | 8 hours | High |
| 9/16/05 | 5 | 4 hours | High |
| 9/17/05 | 6 | 4 hours | High |
| 9/18/05 | 7 | 8 hours | Low |
| 9/19/05 | 8 | 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.

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% O₂. 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 Jet-REMPI results. If discrepancies of greater than 30% were observed, the data were flagged and the samples treated as independent samples for comparison to the Jet-REMPI.

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 Jet-REMPI 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 sampling periods of either 4 or 8 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 Jet-REMPI. Data completeness was reported in terms of the percentage of acceptable samples collected during the verification test and in terms of percentage of time that the Jet-REMPI system was collecting samples compared with the Method 23 sampling trains.

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, except as noted in Section 4.1.2.

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 Jet-REMPI during this verification test.

5.1 Relative Accuracy

The RA of the Jet-REMPI 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 Jet-REMPI 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 Jet-REMPI 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 Jet-REMPI and reference method results for test run i ,
 X_i = the average of the paired Jet-REMPI 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 Jet-REMPI 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 Jet-REMPI 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 ₂ Conc. (%) | CO ₂ Conc. (%) | H ₂ 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 | 8 | High | 305.5 | 4.30 | 12.98 | 11.1 |
| 4 | 9/15/2005 | 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 | 8 | Low | 303.0 | 4.80 | 12.36 | 11.9 |
| 8 | 9/21/2005 | 8 | Low | 305.5 | 3.12 | 13.35 | 11.7 |
| 9 | 9/22/2005 | 8 | High | 315.5 | 3.38 | 13.04 | 11.1 |

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 PCDD/PCDF congeners. The lower portion of the table summarizes the TEQ values for each test run according to PCDDs, PCDFs, and the total. All results have been corrected to 7% O₂.

Table 6-2. Reference 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 [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 |

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 from 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, the average of the results was used in all cases for evaluation of the Jet-REMPI.

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 results of the Jet-REMPI data in terms of the TEQ values for the total PCDD/Fs determined by the Jet-REMPI. These results are derived from the measured concentrations of indicator compounds that the vendor had previously correlated with PCDD/F concentrations. As with the results from the reference method samples, the Jet-REMPI results have been corrected to 7% O₂. The Jet-REMPI results are presented along with the averaged result from the reference method for each test run. The percent difference between the reference method results and the Jet-REMPI results is shown for each test run. The Jet-REMPI results were lower than the reference method results for some test runs and higher for others. The percent differences range from -47.8% to 296% for all the test runs. For Test Runs 6 through 9, a Perma-pure dryer was added to the sampling line to dry the flue gas prior to analysis in an effort to avoid clogging the pulsed valve on a parallel Jet-REMPI unit with condensed water vapor. The parallel Jet-REMPI unit was not evaluated in this verification test but was used throughout the test to monitor for other chemical species in the flue gas.

Table 6-4. Summary of Total PCDD/F Results from the Method 23 Samples and Jet-REMPI

| Test Run | Method 23 Results (ng TEQ/dscm) | Jet-REMPI Results (ng TEQ/dscm) | Difference (ng TEQ/dscm) | Percent Difference |
|------------------|------------------------------------|---------------------------------------|-----------------------------|-----------------------------|
| 1 | 1.62 | 6.42 | 4.80 | 296% |
| 2 | 1.10 | 3.20 | 2.10 | 190% |
| 3 | 6.01 | 6.01 | 0.00 | -0.1% |
| 4 | 5.90 | 5.54 | -0.36 | -6.2% |
| 5 | 5.23 | 4.34 | -0.89 | -17.0% |
| 6 ^(a) | 4.55 | 5.93 | 1.38 | 30.2% |
| 7 ^(a) | 1.20 | 3.03 | 1.83 | 152% |
| 8 ^(a) | 0.90 | 1.77 (5.21) ^(b) | 0.87 (4.31) ^(b) | 96.0% (479%) ^(b) |
| 9 ^(a) | 3.89 | 2.03 | 1.86 | -47.8% |

^(a) Test run conducted with Perma-pure dryer on sample inlet line.

^(b) Values in parentheses indicate results without Perma-pure dryer installed. This value was not included in the calculation of RA.

Table 6-5 shows the relative accuracy results for the Jet-REMPI, expressed as a percent as calculated by Equation (1) (Section 5.1). 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. In addition, the intermethod RSD of the differences between the Jet-REMPI and average of the Method 23 results is shown along with the intramethod RSD between the two Method 23 trains.

Table 6-5. Relative Accuracy Results for the Jet-REMPI

| Parameter | Results |
|-----------------|---------|
| RA | 78.2% |
| Intermethod RSD | 61.5% |
| Intramethod RSD | 8.4 % |

6.2 Range

The range of the Jet-REMPI 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. The greatest absolute percent difference between the Jet-REMPI and Method 23 results was 296% and the lowest absolute percent difference was 0.1%. In general, the Jet-REMPI results showed better agreement with the Method 23 results at high concentrations. At high PCDD/F concentrations (i.e., > 2 ng TEQ/[cubic meter] m³), the average of the absolute percent differences between the Jet-REMPI and the Method 23 results was 20.3%. However, at low PCDD/F concentrations (e.g., < 2 ng TEQ/m³), the Jet-REMPI shows an average absolute difference of 183% relative to the reference method.

Table 6-6 summarizes the test results by sampling duration. In general, the results of Jet-REMPI agreed more closely with the Method 23 results for the 8-hour test runs compared with the 4-hour test runs. The average absolute percent difference for 4-hour test runs was 133%, whereas the average absolute percent difference for the 8-hour test runs was 60.4%.

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

| Duration | Test Run | PCDD/F % Diff |
|---|----------|---------------|
| 8 hr | 3 | -0.1% |
| 8 hr | 4 | -6.2% |
| 8 hr | 7 | 152% |
| 8 hr | 8 | 96.0% |
| 8 hr | 9 | -47.8% |
| 8-Hour Average Absolute % Difference | | 60.4% |
| 4 hr | 1 | 296% |
| 4 hr | 2 | 190% |
| 4 hr | 5 | -17.0% |
| 4 hr | 6 | 30.2% |
| 4-Hour Average Absolute % Difference | | 133% |

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 Jet-REMPI was 100% for the verification test. However, as described in Section 6.4, during one of the Method 23 test runs, the Jet-REMPI sampled the flue gas for only 4 hours of the 8-hour duration of the test run. Thus, the Jet-REMPI collected samples during 93% of the duration of the test runs (i.e., 4 hours downtime divided by 56 hours of test run sampling time = 7.1% downtime).

6.4 Operational Factors

Table 6-7 summarizes the activities performed on the Jet-REMPI system during the verification test, as well as the time required to perform those activities and the amount of downtime experienced to complete those activities. Reported times for instrument start-up, calibration, testing preparations, and instrument shut-down are approximations based on operator experience. Since these operations are relatively complex and may vary depending on day-to-day variability in instrument operation, it is difficult to quantify exactly the time required to complete the necessary activities on a daily basis. Delays in start times of individual test runs were not included in the estimated times although the Jet-REMPI operator continued to perform these activities until each test run commenced.

Table 6-7. Activity Summary for Jet-REMPI

| Date | Duration | Activity | Down Time |
|-------------|------------------------|--|-------------------|
| 9/12/05 | Approximately 7 hours | <ul style="list-style-type: none"> • Instrument start-up, calibration, testing preparations. • Sample collection, desorption, and analysis.^(a) • Instrument shut-down. | NA ^(b) |
| 9/13/05 | Approximately 7 hours | <ul style="list-style-type: none"> • Instrument start-up, calibration, testing preparations. Sample collection, desorption, and analysis.^(a) • Instrument shut-down. | NA ^(b) |
| 9/14/05 | Approximately 10 hours | <ul style="list-style-type: none"> • Instrument start-up, calibration, testing preparations. • Sample collection, desorption, and analysis.^(a) • Instrument shut-down. | NA ^(b) |
| 9/15/05 | Approximately 10 hours | <ul style="list-style-type: none"> • Instrument start-up, calibration, testing preparations. • Sample collection, desorption, and analysis.^(a) • Instrument shut-down. | NA ^(b) |
| 9/15/05 | Approximately 4 hours | Maintenance performed on pulsed valve on a parallel Jet-REMPI unit. ^(c) | 4 hours |
| 9/16/05 | Approximately 2 hours | Maintenance performed on pulsed valve on a parallel Jet-REMPI unit prior to testing. ^(c) | NA |
| 9/16/05 | Approximately 4 hours | <ul style="list-style-type: none"> • Instrument start-up, calibration, testing preparations. • Sample collection, desorption, and analysis.^(a) | NA ^(b) |
| 9/18/05 | Approximately 6 hours | <ul style="list-style-type: none"> • Instrument start-up, calibration, testing preparations. • Sample collection, desorption, and analysis.^(a) • Instrument shut-down. | NA ^(b) |
| 9/19/05 | Approximately 10 hours | <ul style="list-style-type: none"> • Instrument start-up, calibration, testing preparations, and instrument diagnostics. • Sample collection, desorption, and analysis.^(a) • Instrument shut-down. | NA ^(b) |
| 9/21/05 | Approximately 10 hours | <ul style="list-style-type: none"> • Instrument start-up, calibration, testing preparations, and instrument diagnostics. • Sample collection, desorption, and analysis.^(a) • Instrument shut-down. | NA ^(b) |
| 9/22/05 | Approximately 6 hours | <ul style="list-style-type: none"> • Instrument start-up, calibration, testing preparations, and instrument diagnostics. • Sample collection, desorption, and analysis.^(a) • Instrument shut-down. | NA ^(b) |

^(a) Operator was present during entire test run to manually record certain data and to adjust instrument settings as needed.

^(b) NA = Not applicable. Sample installation and recovery are performed outside of sampling period.

^(c) Parallel Jet-REMPI unit was not evaluated in this verification test and was used to independently monitor for other chemical species in the flue gas.

6.4.1 Ease of Use

Ease of use of the Jet-REMPI was established during this verification test based on observations of Battelle staff during the verification testing and through discussions with the operator of the Jet-REMPI. The Jet-REMPI system was installed by representatives of ARCADIS who are on-site contractors to EPA. Installation of the Jet-REMPI was conducted prior to testing and could not be verified by Battelle. Operation of the Jet-REMPI during this verification test was conducted by a single representative of ARCADIS. Operation of the Jet-REMPI requires extensive knowledge of sophisticated laser systems and mass spectrometers, including advanced electronic data collection and manipulation equipment. During the verification test, the operator of the Jet-REMPI was a Ph.D. chemist/physicist with several years of experience with the Jet-REMPI system.

6.4.2 Maintenance

For the purpose of this verification report, sample installation/recovery and system setup were not considered maintenance activities. Outside of routine sample installation/recovery and system set-up, the only maintenance performed on the Jet-REMPI during the verification test involved repairing a faulty pulsed valve on a parallel Jet-REMPI unit. The parallel Jet-REMPI unit was not evaluated in this verification test and was used to monitor for other chemical species in the flue gas. This maintenance resulted in approximately four hours of instrument downtime during one of the test runs.

6.4.3 Consumables/Waste Generation

During the verification test, the Jet-REMPI required the use of small amounts of compressed nitrogen gas and calibration gas standards as consumable materials.

Chapter 7 Performance Summary

Table 7-1 presents a summary of the results of the verification of the Jet-REMPI system during this verification test.

Table 7-1. Summary of Verification Test Results for Jet-REMPI

| Parameter Evaluated | Method of Evaluation | Results | |
|-----------------------------|---|---|-------|
| Relative accuracy | Comparison to Method 23 reference samples | RA | 78.2% |
| | | Intermethod RSD | 61.5% |
| | | Intramethod RSD | 8.4% |
| Range | Comparison to Method 23 reference samples | <ul style="list-style-type: none"> • Apparent dependence of accuracy on PCDD/F TEQ over range of approximately 1 to 6 ng TEQ/dscm with better agreement at high concentration • Apparent dependence of accuracy on sample duration over range of 4 to 8 hours with better agreement for longer sampling duration | |
| Data completeness | Ratio of number of samples successfully collected to number of potential samples that could have been collected | <ul style="list-style-type: none"> • 100% completeness in number of samples collected • Approximately 7% downtime | |
| Ease of use | Operator observations | <ul style="list-style-type: none"> • Time required for installation of the Jet-REMPI system was not verified • During routine operation, a representative of ARCADIS was on-site and constantly monitoring instrument diagnostic and indicator signal. • Extensive training and experience with advanced knowledge of mass spectrometry and laser spectroscopy techniques is required for operation of the Jet-REMPI and interpretation of the results | |
| Maintenance | Verification test staff observations | Repair of a faulty pulsed valve on a parallel Jet-REMPI unit was required during the verification test. The maintenance activities resulted in approximately 4 hours of instrument downtime. | |
| Consumables/waste generated | | Small amounts of compressed gas and calibration gas standards were used during the verification test. | |

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.