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Environmental Technology Verification Program

Advanced Monitoring Systems Center

Test/QA Plan for Verification of
Dioxin Emission Monitoring Systems
(EMSs)

ETV ETV ETV

TEST/QA PLAN

for

Verification of
Dioxin Emission Monitoring Systems (EMSs)

Version 1.0

September 2, 2005

Prepared by

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SECTION A
PROJECT MANAGEMENT

A1 VENDOR APPROVAL PAGE

ETV Advanced Monitoring Systems Center

Draft Test/QA Plan for Verification of
Dioxin Emission Monitoring Systems (EMSs)

Version 1

September 2, 2005
APPROVAL:

Name _____

Company _____

Date _____

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A4 VERIFICATION TEST ORGANIZATION

The verification test will be conducted under the auspices of the U.S. Environmental Protection Agency (EPA) through the Environmental Technology Verification (ETV) Program. It will be performed by Battelle, which is managing the ETV Advanced Monitoring Systems (AMS) Center through a cooperative agreement with EPA. The scope of the AMS Center covers verification of monitoring technologies for contaminants and natural species in air, water, and soil.

This verification test will be coordinated and supervised by Battelle, with the support of ARCADIS Inc., and in cooperation with EPA. The testing will be conducted at the EPA's Research Triangle Park (RTP) campus and will involve the evaluation of commercial dioxin emission monitoring systems (EMSs), where the term "dioxin" is used to generically represent polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. Staff from ARCADIS will support this test under subcontract from Battelle. ARCADIS will provide support in preparing for the test, during installation of the dioxin EMSs to be tested, and by overseeing operation of the EMSs during periods of routine operation. Additionally, ARCADIS will collect reference dioxin samples and will arrange for the reference samples to be analyzed using a modified version of EPA Method 23.[1]

Each EMS vendor will install their respective EMS, operate the EMS through portions of the test (unless they give written consent for Battelle or ARCADIS staff to operate it), and repair or maintain their EMS during the test.

Quality assurance (QA) oversight will be provided by the Battelle Quality Manager, and also by the EPA AMS Center Quality Manager at her discretion. The organization chart in Figure 1 identifies the responsibilities of the organizations and individuals associated with the verification test. Roles and responsibilities are defined further below.

Battelle Management		Battelle AMS Center Manager		EPA AMS Center Manager	
		Karen Riggs		Robert Fuerst	

Battelle Quality Manager			EPA Quality Manager	
Zachary Willenberg			Elizabeth Betz	

Verification Testing Leader
Thomas Kelly

EPA Technical Facilitator		Verification Test Coordinator		Vendor Representatives
C.W. Lee		Kenneth Cowen		

Battelle Testing Staff

ARCADIS QA Officer		ARCADIS Technical Lead		ARCADIS Safety Officer
Laura Nessley		Dahman Touati		Jerry Revis

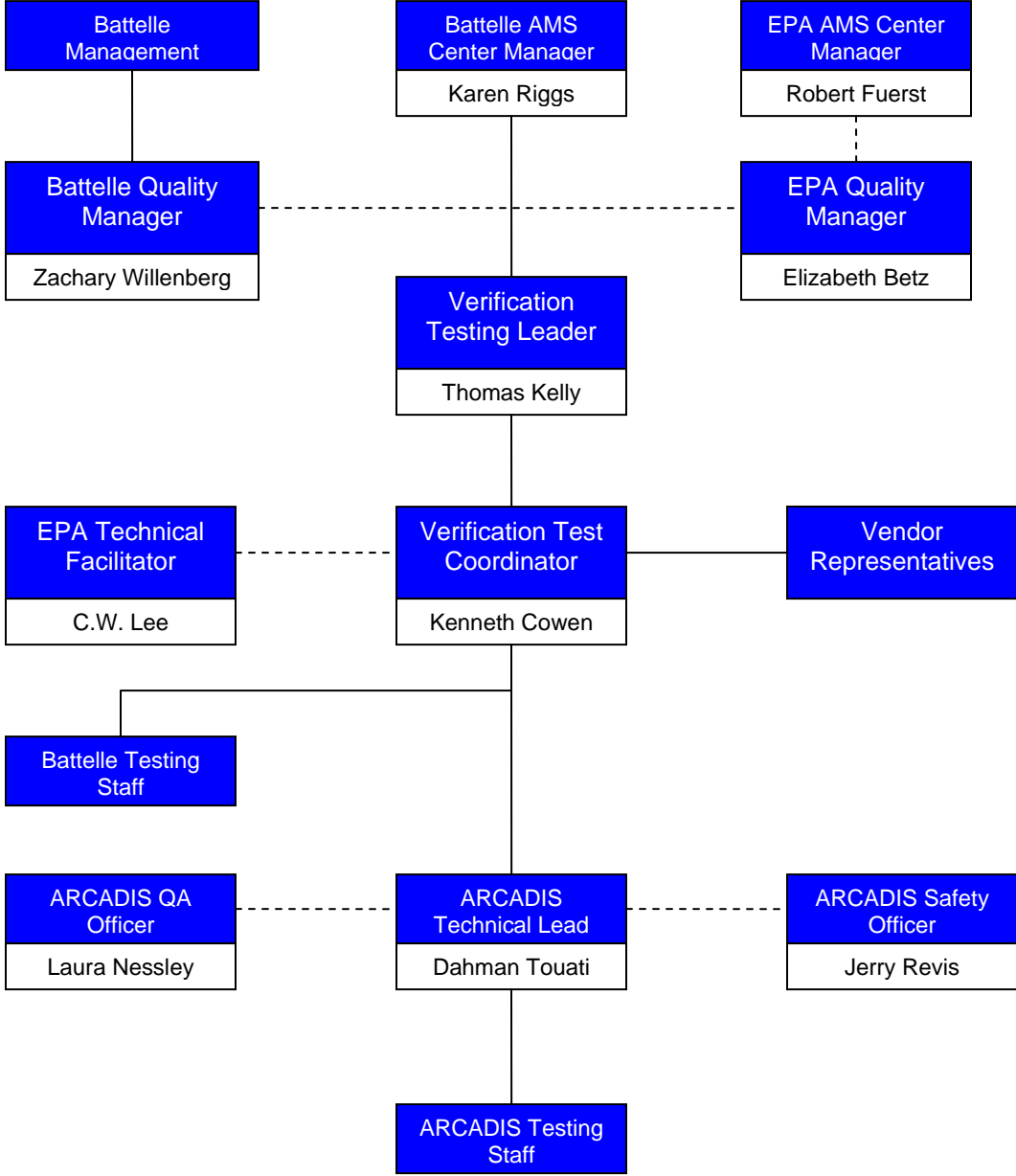| ARCADIS Testing Staff |
|---|

Figure 1. Organizational Chart

A4.1   Battelle

Dr. Kenneth Cowen is the AMS Center Verification Test Coordinator for this test. In this role, Dr. Cowen will have overall responsibility for ensuring that the technical, schedule, and cost goals established for the verification test are met. Specifically, he will:

➢ Assemble a team of qualified technical staff to conduct the verification test.

➢ Direct the team (Battelle and ARCADIS staff) in performing the verification test in accordance with this test/QA plan.

➢ Ensure that all quality procedures specified in the test/QA plan and in the AMS Center Quality Management Plan[2] (QMP) are followed.

➢ Manage the subcontract(s) under which ARCADIS conducts the testing activities.

➢ Prepare the draft and final test/QA plan, verification reports, and verification statements.

➢ Revise the draft test/QA plan, verification reports, and verification statements in response to reviewers' comments.

➢ Respond to any issues raised in assessment reports and audits, including instituting corrective action as necessary.

➢ Serve as the primary point of contact for vendor representatives.

➢ Coordinate distribution of the final test/QA plan, verification reports, and statements.

➢ Establish a budget for the verification test and manage staff to ensure the budget is not exceeded.

➢ Ensure that confidentiality of sensitive vendor information is maintained.

Dr. Thomas Kelly is Battelle's Verification Testing Leader for the AMS Center. Dr. Kelly will:

➢ Support Dr. Cowen in preparing the test/QA plan and organizing the test.

➢ Review the draft and final test/QA plan.

➢ Review the draft verification reports and statements.

➢ Support Dr. Cowen in responding to any issues raised in assessment reports and audits.

Ms. Karen Riggs is Battelle's manager for the AMS Center. Ms. Riggs will:

➢ Review the draft and final test/QA plan.

➢ Review the draft and final verification reports and verification statements.

➢ Ensure that necessary Battelle resources, including staff and facilities, are committed to the verification test.

➢ Ensure that confidentiality of sensitive vendor information is maintained.

➢ Maintain communication with EPA's technical and quality managers.

➢ Facilitate a stop work order if Battelle or EPA QA staff discovers adverse findings that will compromise data quality or test results.

Battelle Testing Staff will conduct the testing of the dioxin EMSs during the verification test. Battelle staff (including Dr. Cowen) will be on-site at the EPA test facility during the verification test, and will be in daily communication with facility personnel, and with EMS vendors as needed. The responsibilities of the technical staff will be to:

➢ Maintain and operate the dioxin EMSs if so instructed by the vendors, assuming proper training in EMS operation is provided.

➢ Assure that verification testing is performed as described in the test/QA plan.

➢ Communicate and coordinate with ARCADIS staff and the EMS vendor representatives on the installation, operation, testing, and removal of the EMSs.

➢ Communicate with ARCADIS testing staff on the planning, performance, and reporting of the reference dioxin sampling and analysis.

➢ Record qualitative observations about the maintenance and operation of the dioxin EMSs during testing.

> ➢ Assure that the data from each dioxin EMS are recorded and transmitted to the Verification Test Coordinator on at least a weekly basis.

> ➢ Provide input on test procedures, EMS operation and maintenance, and field conditions for the draft verification reports.

<u>Mr. Zachary Willenberg</u> is Battelle's Quality Manager for the AMS Center. Mr. Willenberg will:

> ➢ Review the draft and final test/QA plan.
> ➢ Conduct a technical systems audit at least once during the verification test, or designate other QA staff to conduct the audit.
> ➢ Audit at least 10% of the verification data.
> ➢ Prepare and distribute an assessment report for each audit.
> ➢ Verify implementation of any necessary corrective action.
> ➢ Notify Battelle's AMS Center Manager to issue a stop work order if audits indicate that data quality is being compromised.
> ➢ Provide a summary of the QA/QC activities and results for the verification reports.
> ➢ Review the draft and final verification reports and verification statements.
> ➢ Assume overall responsibility for ensuring that the test/QA plan is followed.

A4.2 Dioxin EMS Vendors

The responsibilities of the EMS vendors are as follows:

> ➢ Review and provide comments on the draft test/QA plan.
> ➢ Approve the final test/QA plan prior to test initiation.
> ➢ Provide a dioxin EMS with complete flue gas sampling inlet for evaluation during the verification test.
> ➢ Provide all other equipment/supplies/reagents/consumables needed to operate their EMSs for the duration of the verification test.

➢ Supply a representative to install and maintain their technology, and to operate it in portions of the test specified in this test/QA plan, or provide written consent and instructions for Battelle staff to carry out these activities.

➢ Provide written instructions for routine operation of their EMSs, including a daily checklist of diagnostic and/or maintenance activities.

➢ Review and provide comments on the draft verification report and statement for their respective EMSs.

A4.3   EPA

EPA's responsibilities for the AMS Center are based on the requirements stated in the "Environmental Technology Verification Program Quality Management Plan" (EPA QMP).[3] The roles of specific EPA staff are as follows:

Ms. Elizabeth Betz is EPA's AMS Center Quality Manager. Ms. Betz will:

➢ Review the draft test/QA plan.
➢ Perform at her option one external technical systems audit during the verification test.
➢ Notify the EPA AMS Center Manager of the need for a stop work order if the external audit indicates that data quality is being compromised.
➢ Prepare and distribute an assessment report summarizing results of the external audit.
➢ Review draft verification reports and statements.

Mr. Robert Fuerst is EPA's manager for the AMS Center. Mr. Fuerst will:

➢ Review the draft test/QA plan.
➢ Approve the final test/QA plan.
➢ Review the draft verification reports and statements.
➢ Oversee the EPA review process for the verification reports and statements.

➢ Coordinate the submission of verification reports and statements for final EPA approval.

A4.4 ARCADIS

ARCADIS personnel are responsible for performing most of the actual testing activities, including providing required emissions sampling and analytical services. In addition, ARCADIS will purchase incidental materials as needed for the verification test, as well as provide repair and preventive maintenance support to equipment at the host facility that will be used during the verification test.

Dr. Dahman Touati is the ARCADIS Technical Lead for the dioxin EMS verification test. In this role, Dr. Touati is responsible for ensuring that the project meets the scheduled technical milestones agreed upon by Battelle through subcontracts with ARCADIS. Dr Touati will:

➢ Be the primary ARCADIS contact for Battelle's Verification Test Coordinator.

➢ Ensure that designated ARCADIS staff, and the EPA test facility are ready for the verification test.

➢ Coordinate distribution of the test/QA plan to ARCADIS staff.

➢ Coordinate the operations of the boiler and testing facilities.

➢ Direct the ARCADIS testing staff in performing the baseline testing in accordance with the test/QA plan.

➢ Review and approve all data and records related to facility operation

➢ Review the draft test/QA plan.

➢ Assist Battelle and EMS vendor staff in the installation, operation, testing, and removal of the EMSs at the EPA boiler facility, including connection of EMS flue gas sampling inlets to the facility stack.

➢ Assist in the planning and performance of the reference dioxin sampling and analysis.

➢ Ensure the availability of appropriate space and needed utilities (e.g., electricity, air, water) for the EMSs during testing.

➤ Support Battelle Testing Staff in providing daily oversight of the EMSs during periods of routine operation, checking diagnostic indicators and contacting Battelle if faults in EMS operation are observed.

➤ Support Battelle Testing Staff in recording observations about the maintenance and operation of the dioxin EMSs during the test period.

➤ At the option of EPA facility staff, review the draft verification reports and statements.

➤ Coordinate with the ARCADIS QA and safety officers to ensure appropriate procedures are in place and followed during the verification test.

The responsibilities of <u>ARCADIS Testing Staff</u> in this test are as follows:

➤ Provide equipment and personnel to carry out dioxin reference sampling using Method 23 sampling trains as described in this test/QA plan.

➤ Recover collected samples from the Method 23 trains, and transfer the recovered samples for dioxin analysis.

➤ Coordinate analysis on flue gas samples and QA samples per the modified Method 23 described in this test/QA plan.

➤ Calculate the Method 23 sampling results in terms of flue gas dioxin concentrations as specified in the method, and submit a report to Battelle that describes the sampling, and presents the sample analysis results, QA results, and calculated dioxin concentrations in the flue gas

➤ Review that portion of the verification reports that describes the Method 23 sampling and analysis.

The ARCADIS QA Officer is <u>Laura Nessley</u> who is responsible for:

➤ Reviewing and approving procedures and testing performed by ARCADIS and described in this QAPP.

➢ Ensuring that the ARCADIS portion of the QAPP is implemented by performing routine assessments.

➢ Communicating with Battelle's Quality Manager for the AMS center to coordinate any planned audits.

The ARCADIS Safety Officer is <u>Jerry Revis</u>. Mr. Revis will be responsible for:

➢ Ensuring that this project is carried out in accordance with all permit and EPA safety requirements.

➢ Ensuring that anyone working on the project has fulfilled all of the safety training requirements.

A5   BACKGROUND

The ETV Program's AMS Center conducts third-party performance testing of commercially available technologies that detect or monitor natural species or contaminants in air, water, and soil. Stakeholder committees of buyers and users of such technologies recommend technology categories, and technologies within those categories, as priorities for testing. Dioxin EMSs were identified as a priority technology category through the AMS Center stakeholder process, since these emerging technologies have significant potential to improve upon the standard method for the determination of dioxins in flue gas.

EPA Method 23[1] is the certified extractive method used for quantification of 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 (~once each year) for compliance purposes and not for long-term or short-term performance monitoring. New 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. 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 is to generate performance data on dioxin EMS technologies so organizations and users interested in installing and operating dioxin EMSs on their municipal waste incinerators and industrial plants can be assured of their benefit. The test will be conducted over a period of approximately two weeks and will involve the continuous operation of several dioxin EMSs at a well-controlled, pilot-scale boiler facility located at EPA laboratories in Research Triangle Park, North Carolina. The accuracy and range of the EMSs will be determined through comparisons to the standard EPA integrated sampling method for dioxin. Other performance parameters such as data completeness, maintenance requirements, ease of use, and operational costs will be determined from operator observations. This test is not intended to simulate long-term performance of these technologies on a full-scale incinerator or plant.

A6   VERIFICATION TEST DESCRIPTION AND SCHEDULE

A6.1 Verification Test Description
In general, the dioxin EMS technologies to be evaluated in this verification test can be categorized into two groups:

(1) technologies that collect long-term integrated samples of dioxin from flue gas onto sorbent media, for subsequent laboratory analysis, and

(2) technologies that allow for continuous or semi-continuous sampling and automated, on-site analysis of dioxins or marker compounds using in-situ laser ionization/mass spectrometric techniques.

Typically, the technologies which collect integrated samples for laboratory analysis consist of a sampling unit which mounts to the duct and isokinetically samples the flue gas, and a control unit that remotely controls the gas sampling based on pre-set sampling times. In addition to

sample collection, these systems can be configured to measure a variety of flue gas parameters and can be programmed to automatically stop sampling in the event of unusual operating conditions. After sampling, the sample media are retrieved and sent to a laboratory for analysis.

The operating principles of the laser-ionization/mass spectrometric technologies include laser-induced ionization of a molecule of interest using a multi-step resonant process, followed by mass spectrometric measurement of the resulting ions. Typically, this process involves absorption of a single ultra violet (UV) photon followed by the subsequent absorption of a second UV photon to bring the internal energy of the molecule above its ionization energy, and resulting in the formation of a molecular ion. After ionization, the created ions are extracted into a time-of-flight (TOF) mass spectrometer and detected. Generally, the spectral absorption "fingerprint" of a specific molecule/ion is sufficiently unique for unambiguous identification of target molecules and can be obtained by systematically changing the wavelength of the laser radiation.

This verification test will involve the simultaneous evaluation of multiple dioxin EMSs under realistic operating conditions on a pilot-scale boiler. The EMSs will be operated for approximately two weeks, during which time a series of Method 23 reference samples will be collected. The operational parameters of the boiler will be systematically varied during testing to provide a range of expected dioxin concentrations in the flue gas.

In performing the verification test, Battelle will follow the technical and QA procedures specified in this test/QA plan and will comply with the data quality requirements in the AMS Center QMP.[2]

A6.2   Verification Test Schedule

Table A1 shows the planned schedule of testing and data analysis/reporting activities to be conducted in this verification. The verification test of dioxin EMSs is planned to be conducted in September 2005, with installation of the EMSs at the host facility in late August 2005.

Table A1. Planned Verification Test Schedule

Date(s)	Testing Activities	Data Analysis and Reporting
August 29- September 9	Set up/install EMSs EMS shakedown	Begin preparation of report template
September 12- September 23	Routine operation Reference sampling periods Remove EMSs from host facility Begin analysis of first reference samples	Review and summarize operator observations Compile data from EMSs
October 30	Complete analysis of reference samples	Complete common sections of reports
November 30		Complete draft reports Vendor review of draft reports
January 30, 2006		Revise draft reports Peer review of draft reports Submit final reports for EPA approval

Subsequent to the verification test, a separate verification report will be drafted for each EMS. These reports will be reviewed by the respective vendors and by peer reviewers, and submitted to EPA for final signature. The period of operation of the EMSs at the facility will be approximately 2 weeks. Installation of the EMSs is expected to begin during the week of August 29, 2005 and is expected to be completed by September 9. Routine operation of the EMSs is expected to begin on September 12 and continue until September 23, 2005, or until all testing activities are completed. During testing, it is anticipated that at least one set of reference samples will be collected each day. Depending on timing, more than one set of reference samples may be collected in one day.

The test procedures are described in Section B of this test/QA plan. Changes in the operational conditions of the boiler will be introduced to provide a range of expected dioxin concentrations in the flue gas.

A6.3 Test Facility

A 2.94 MBtu/hr, 3-Pass Wetback Scotch Marine Packaged Boiler (SMPB) manufactured by Superior Boiler Works, Inc., and located at the EPA RTP facility, will be used for the verification test. This boiler is capable of firing natural gas or a variety of fuel oils. The oil burner used is a low pressure, air atomizing nozzle that delivers a fine spray at an angle which

ensures proper mixing with the air stream. The burner can be set to fire automatically or manually at any desired rate between the minimum and the maximum firing rates. Fuel oil temperature can be adjusted using an electric heater to maintain proper viscosity; the fuel and atomizing airflow rates are variable to ensure adequate oil atomization. The boiler has 33-square meters of heating surface and generates up to 1,090 kg/hr of saturated steam at pressures up to 15 psig. Fuel flows are measured with a liquid volume totalizer and stoichiometric ratios are verified through O_2 and CO_2 emission concentrations. The SMPB is shown in Figure 1.

During this verification test, the SMPB will be fully instrumented with continuous emission monitors (CEMs) for a variety of species including O_2, CO, H_2O, HCl, and SO_2. Continuous emission monitoring of chemical species is performed with two shared CEMs for the package boiler facility. The first CEM bench includes four gas analyzers: high range CO, low range CO, O_2, and CO_2, each with multiple ranges. HCl, and SO_2, on the other hand, will be measured by a self-contained bench-scale CEM system (Bodenseewerk). The system uses an Altech Hot/Wet (HW) sampling system and a Perkin-Elmer (PE) MCS-100 Infrared (IR) 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 compounds that can be measured include HCl, NH_3, N_2O, H_2O, NO_2, CO, CO_2, and SO_2. The HW probe assembly provides functions for reliable sampling of flue gases, while closely maintaining temperatures at elevated levels. The functions include probe blowback with instrument air, calibration gas injection, and processes to protect the system from corrosion. The Altech HW sampling system is designed to maintain elevated temperatures, up to 250 °C, throughout the entire gas analyzer. Monitored concentrations are continuously output as linear 4-20 mA signals.
.
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 is equipped with several sampling ports located at the exit of the boiler. The vertical section of the duct (8 in. steel pipe) is sufficient in length and free of flow

Figure 1. Wetback Scotch Marine Packaged Boiler

disturbances so that particulate matter can be sampled at an axial location that meets EPA Method 1A particulate matter sampling requirements. Several sampling ports are located along the horizontal section of duct approximately 3 meters above the facility catwalk. The horizontal section of the duct (20 cm. steel pipe) is also sufficient in length and free of flow disturbances so that particulate matter can be sampled at an axial location that meets EPA Method 1A particulate matter sampling requirements. The boiler stack has been modified to accommodate sampling stations for each of the EMSs and for Method 23 sampling trains.

A surrogate chlorinated chemical (1,2-dichlorobenzene) and a source of metal atoms (copper naphthenate) will be added to the boiler fuel to promote dioxin formation for the EMS testing.[4] 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 consists of a 37 liter pressurized stainless steel tank, in

which the surrogate and the copper naphthenate are mixed. A series of check valves were incorporated in the feed system to avoid contaminating the fuel oil recirculation in case of an accidental shutdown of the boiler, as well as a flow meter for measurement of the feed flow rate. A solenoid valve electrically tied to the burner management/safety system is included to stop any surrogate feed to the burner when the burner is off. The pressurized stainless steel tank is contained in a secondary container to minimize any spill that may occur during the surrogate addition process. The amount of copper to be injected with the surrogate is calculated to simulate the copper content in ash of refuse-derived fuel, generating approximately 20% ash and an estimated concentration of copper of 100 mg per kg of ash. Since the mixture is prepared for different test conditions, the concentration of copper injected varies with the surrogate injection rate, the chlorine content in the boiler being the main driver. This injection rate is determined by the calculated HCl concentration to be maintained in the flue gas. Prior to testing, the boiler emissions were characterized under a series of test conditions similar to those that will be used in the verification test. The results of the boiler characterization are presented below.

Table A2 summarizes the characteristics of the flue gas from the EPA boiler at the point where the dioxin EMSs will be installed. These characteristics show the average and the range of several key constituents.

Table A2. Stack Gas Characteristics of the EPA SMPB

Parameter	Typical Value	Range or Maximum
O_2(%)	2.2	0.5 – 4.0
CO_2 (%)	13.2	12 – 15
CO (ppm)	230	5 – 650
Calculated HCl (ppm)	463	35 – 1150
Total TEQ[a] (TEQ/dscm)	15.2	1.6 – 56

[a]   TEQ – Toxic Equivalents

A7   QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

The objective of this verification test is to evaluate the performance of dioxin EMSs under realistic operating conditions. This evaluation will in part assess the capabilities of the dioxin EMSs for determining dioxins in the flue gas of a boiler which is cofiring copper napthenate and dichlorobenzene, and will include a comparison of the EMS results to those of reference samples collected by Method 23[1]and analyzed for dioxins according to a modified version of Method 23 as described in Section B4. Additionally, this evaluation will rely upon operator observations to assess other performance characteristics of the EMSs. Below is a discussion of the quality objectives and the criteria for measurement data that have been established to assure that the objectives of this test are met.

A7.1   Quality Objectives

The data quality objectives indicate the minimum quality of data required to meet the objectives of the verification of dioxin EMSs. The data quality objectives for this verification test include those for the collection and analysis of reference samples, those for the operation of the boiler at the test facility and consequently of the flue gas conditions, as well as those for the documentation of operator observations. The data quality objectives for the collection and analysis of the reference samples are based on the requirements of Method 23[1] and the modifications to Method 23 described in Section B4, and are presented in terms of data quality indicators (DQI) criteria for the critical measurements associated with those methods. The data quality of the reference samples relies, in part, on the proper operation of the test boiler, and consequently on the flue gas conditions. As such, data quality objectives for the operation of the boiler have been established for this verification test and are defined in terms of DQI goals for the boiler controls, and for the CEMs which monitor the flue gas conditions. The data quality objectives for the operator observations have not been defined quantitatively but have been incorporated into documentation requirements and data review, verification, and validation requirements for this verification test.

A7.2 Criteria for Measurement Data

Table A3 presents the DQIs and criteria for the critical measurements of the reference method. Table A4 presents the criteria for DQIs for several important but non-critical measurements made by the CEMs at the SMPB facility.

The quality of the reference measurements will be assured by adherence to these DQI criteria and the requirements of Method 23 with the exception of the modifications described in Section B4, including the QA/QC requirements of those methods. The quality of the reference measurements will be monitored by inclusion of blank samples and performance evaluation (PE) samples (Section C1.1) as appropriate. The quality of the data relating to the boiler operation and the flue gas conditions will be assured through the accurate measurement of O_2, CO, H_2O, dopant flow injection rate, and total flue gas flow rate.

Various calibration requirements and QA/QC checks are associated with Method 23 and are discussed in detail in Sections B2-B7 of this test/QA plan. Dioxin standards to be used in calibration standards and QC samples must meet National Institute of Standards and Technology (NIST) traceability, when available. Acceptance criteria for PE samples and PE audit measurements are given in Section C1.1.

The Battelle Quality Manager or his designee will perform a technical systems audit (TSA) at least once during this verification test to augment these QA/QC requirements. The EPA Quality Manager also may conduct an independent TSA, at her discretion.

Table A3. DQIs and Criteria for Critical Measurements for EPA Method 23.

Measurement	DQI	Criteria
Internal standard recovery	Accuracy	Recovery: 40 to 130% for tetra- through hexachlorinated compounds; and 25 to 130% for hepta- and octachlorinated compounds
Surrogate standard recovery	Accuracy	Goal of 70 to 130% recovery, otherwise correction is necessary
Flue gas flow rate	Precision	±5%
Flue gas temperature	Precision	±5 ^{o}C
Flue gas pressure	Precision	±2%
Leak check	Bias	Leak rate of less than 0.02 ft^3/min
Field blanks	Bias	if blank >30% of sample concentration, data must be flagged
GC column performance	Bias	Retention times within 10 seconds of expected retention times
Solution blanks	Bias	Blank <10% of sample concentration or <10 x LOD, subtract blank from samples; if blank >10% of sample concentration, data must be flagged
Duplicate reference samples	Precision	Concentration differences < 30%

Table A4. DQI Goals for SMPB Continuous Emission Monitors

Measurement Parameter	Method	Precision[1] (RSD) (%)	Bias[2] (%)	Completeness (%)
O_2	CEM	<7	<10	>90
CO	CEM	<20	<10	>90
H_2O	CEM	<20	<10	>90

[1]Analyzer precision will be assessed from repeated measurements under nominally constant operation (i.e., during bias testing).

[2]Analyzer bias is assessed daily; it measures the degree of disagreement between an averaged measurement and an accepted reference value, expressed as a percentage of the reference value.

A8   SPECIAL TRAINING/CERTIFICATION

Documentation of training related to technology testing, field testing, data analysis, and reporting is maintained for all Battelle technical staff in training files at their respective locations. Documentation of the expertise and experience of ARCADIS staff in Method 23 sampling and analysis is similarly available. The Battelle Quality Manager may verify the presence of appropriate training records prior to the start of testing. If Battelle or ARCADIS staff operate and/or maintain an EMS during the verification test, the EMS vendor will be required to train those staff prior to the start of testing. Battelle will document this training with a consent form, signed by the vendor that specifies which Battelle/ARCADIS staff have been trained on their EMS. Battelle technical staff will have a minimum of a bachelor's degree in science/engineering or have equivalent work experience.

A9   DOCUMENTATION AND RECORDS

The records for this verification test will include the test/QA plan, chain-of-custody forms, laboratory record books (LRB), data collection forms, electronic files (both raw data and spreadsheets), and the final verification report. All of these records will be maintained at the host facility or in the Verification Test Coordinator's office during the test and may be transferred to permanent storage at Battelle's Records Management Office (RMO) at the conclusion of the verification test. All Battelle LRBs are stored indefinitely, either by the Verification Test Coordinator or Battelle's RMO. EPA will be notified before disposal of any files. The documentation and results of the Method 23 measurements made by ARCADIS will be submitted to Battelle after completion of all sample analyses, review of the data, and calculation of dioxin concentrations in the flue gas. Section B10 further details the data recording practices and responsibilities.

SECTION B
MEASUREMENT AND DATA ACQUISITION

B1   EXPERIMENTAL DESIGN

This test will specifically address verification of EMSs for dioxins in flue gas by evaluating the accuracy and operational range of the EMS measurements, as well as the ease of use, reliability, and maintenance needs of each EMS. Specifically, the dioxin EMSs will be evaluated for the following performance parameters:

- Relative Accuracy
- Range
- Data Completeness
- Operational factors such as maintenance, ease of use, reliability, and operational costs.

Relative accuracy and range will be determined for each EMS by comparison of EMS results to results from Method 23 reference samples collected simultaneously with the EMS measurements. Range will be determined from measurements over a variety of defined operating conditions expected to produce differing levels of dioxins. Data completeness will be assessed as the percentage of maximum data return that is achieved by each EMS over the test period. Operational factors will be evaluated by means of operator observations, and records of needed maintenance, vendor activities, and expendables used.

B1.1   Test Procedures
The following sections describe the test procedures that will be followed during the verification test.

B1.1.1 Relative Accuracy

The relative accuracy of each dioxin EMS will be evaluated by comparison of EMS results to simultaneous results obtained by sampling the flue gas with Method 23. During the verification test a series of nine (9) Method 23 test runs will be conducted using duplicate Method 23 trains. The Method 23 trains will sample from ports located at each end of the sampling region where the EMSs are installed. The reference samples will be recovered and submitted for analysis by the modified version of Method 23 described in Section B4. The dioxin concentrations determined by the reference methods will be compared to corresponding results from each EMS, averaged over the period of each Method 23 test run. During each of the test runs the boiler operation will be maintained as constant as possible based on measurements of the flue gas conditions and boiler control parameters (e.g., dopant injection rate). However, the duration of the sampling periods and the operating conditions of the boiler will be changed from run to run to provide a range of conditions under which the EMSs will be evaluated. Two sets of operating conditions will be used for the test runs to generate expected high and low dioxin concentrations. Test runs of various durations will be conducted under each set of operating conditions. The duration of the sampling periods for the Method 23 test runs will be varied to assess the ability of the EMSs to accurately determine dioxin concentrations over a range of sampling times. Sampling periods of four hours will be used to assess short-term accuracy of the EMSs, whereas long-term accuracy of the EMSs will be assessed from composite samples collected over two 8-hour sampling periods on successive days (i.e., totaling 16 hours per sample). For samples collected over multiple days, the Method 23 trains used for the sample collection will be removed from the duct after each session. The samples will be recovered and analyzed for each 8-hour session. The EMSs that collect long-term samples will be shut off after each 8-hour session but the sampling media may, at the vendor's discretion, remain in place until sampling has been completed for the appropriate number of 8-hour sessions. The results of the long term EMS samples will be compared with the cumulative average of the appropriate 8-hour reference samples. Table B1 shows the sampling durations and boiler operating conditions for each of the test runs, and Table B2 shows a tentative schedule for completion of the test runs. **Note: The test runs may not be completed in the order shown in the tables.**

Table B1. Test Run Summary

Test Run	Sampling Duration	Expected Dioxin Concentration[a]
1	4 hours	Low
2, 3	16 hours (2 x 8 hours)	High
4	4 hours	Low
5	8 hours	Low
6	4 hours	High
7, 8	16 hours (2 x 8 hours)	Low
9	4 hours	High

[a] - Expected concentrations based on results of baseline testing. High corresponds to expected concentrations near the upper end of the range, and low corresponds to expected concentrations near the lower end of the range.

Table B2. Tentative Schedule for Collection of Reference Samples

Test Run	Week 1					Week 2				
	M	T	W	Th	F	M	T	W	Th	F
1	X									
2, 3		X	X							
4				X						
5					X					
6						X				
7, 8							X	X		
9									X	

Two Method 23 trains will be used to collect each reference sample during each test run. These trains will each sample isokinetically from a single point in the gas flow, with one of the trains sampling at each end of the sampling region where the EMSs are sampling. To assure comparability of the EMS and Method 23 results, each reference method sampling run will start no sooner than a time previously agreed upon with the EMS vendors. The vendors, Battelle

staff, and ARCADIS staff will be given at least 15 minutes notice prior to the start of each reference sampling run. However, there will be no obligation to delay the start of a reference method run because of a lack of readiness on the part of an EMS vendor. Vendors will similarly be notified as the end of each Method 23 run approaches, so that they can stop sampling or define the reporting period for data, as appropriate for their EMS.

Upon completion of each test run, the Method 23 trains will be dismantled for sample recovery in the field by ARCADIS staff, and all collected sample fractions will be logged and stored for transfer to the analytical laboratory. All sample handling, QA/QC activities, and dioxin analyses will be conducted by ARCADIS or EPA staff, adhering to all requirements of Method 23 and the modifications described in Section B4 of this test/QA plan. Subsequent to analysis, ARCADIS will review the data, and report final dioxin concentrations from all trains in units of toxic equivalents per dry standard cubic meter (TEQ/dscm), corrected to 7% O_2. The results from the simultaneously collected Method 23 trains will be used to assess the degree of dioxin loss (if any) in the duct between the two reference method sampling ports. Unless discrepancies of greater than 30% are observed for total measured TEQs between the reference samples collected simultaneously, the results from the reference method samples will be averaged together, to produce the final reference data used for comparison to the EMS results. If discrepancies of greater than 30% are observed, the data will be flagged and the samples will be treated as independent samples for comparison to the EMSs.

B1.1.2 Range

No additional test procedures will be carried out specifically to address range. Rather, this parameter will be assessed in terms of relative accuracy over the range of measured dioxin concentrations and sampling periods. The reference method samples will be collected over a range of expected dioxin concentrations in order to assess the degree of agreement of each of the EMSs with the reference method under a range of conditions and sampling times. Based on results from baseline testing of the boiler conducted prior to the verification test, the dopant injection rate and firing conditions will be changed for different Method 23 runs to achieve

different expected dioxin concentrations. Additionally, the duration of the test runs will be varied to achieve a range of sampling periods. The flue gas HCl level will be used as an indicator of the expected dioxin concentrations in the flue gas.

B1.1.3 Data Completeness
No additional test procedures will be carried out specifically to address data completeness. This parameter will be assessed based on the overall data return achieved by each EMS.

B1.1.4 Operational Factors
Operational factors such as maintenance needs, data output, consumables used, ease of use, repair requirements, etc., will be evaluated based on observations recorded by Battelle and facility staff, and in some cases by the EMS vendors. A laboratory record book will be maintained at the test facility, and will be used to enter daily observations on these factors. Examples of information to be recorded in the record books include the daily status of diagnostic indicators for the EMS; use or replacement of any consumables; the effort or cost associated with maintenance or repair; vendor effort (e.g., time on site) for repair or maintenance; the duration and causes of any EMS down time or data acquisition failure; and operator observations about ease of use of the EMS. These observations will be summarized to aid in describing EMS performance in the verification report on each EMS.

B1.2   Statistical Analysis
The statistical methods and calculations used for evaluation of the quantitative performance parameters are described in the following sections.

B1.2.1 Relative Accuracy
The relative accuracy (RA) of the EMSs with respect to the reference sample results will be assessed as a percent bias, using Equation 1:

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

where:

$\left|\overline{d}\right|$ = the absolute value of the mean of the differences between the EMS and

reference sample results for each test run,

$t_{0.975}$ = the *t*-value,

S_d = the standard deviation of the differences between the EMS and reference sample

results for each test run, and

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

B1.2.2 Range
The measurement range of the EMSs will be reported in terms of the accuracy of the EMSs relative to the reference method under the variety of boiler operating conditions and sampling durations used during the test runs.

B1.2.3 Data Completeness
Data completeness will be calculated as the percentage of the total possible data return over the entire field period that is achieved by each EMS. For each EMS that collects real-time data this calculation will use the total hours of data recorded, divided by the total hours of data in the entire field period. For EMSs that collect integrated samples, data completeness will be assessed in terms of the percentage of successfully recovered samples collected during the corresponding test runs. The causes of any substantial incompleteness of data return will be established from operator observations or vendor records, and noted in the discussion of data completeness results.

B1.3   Reporting

The statistical comparisons described above will be conducted separately for each of the EMSs being tested, and information on the operational parameters will be compiled and reported. The data for each EMS will be kept separate from data for all other EMSs, and no intercomparison of the data from different EMSs will be performed at any time. A separate verification report will be prepared for each EMS tested, that presents the test procedures and test data, as well as the results of the statistical evaluation of those data.

Operational aspects of the EMSs will be recorded by testing staff at the time of observation during the field test, and summarized in the verification report. For example, descriptions of the data acquisition procedures, use of vendor-supplied proprietary software, consumables used, repairs and maintenance needed, and the nature of any problems will be presented in the report. Each verification report will briefly describe the ETV program, the AMS Center, and the procedures used in verification testing. The results of the verification test will be stated quantitatively, without comparison to any other EMS tested, or comment on the acceptability of the EMS's performance. Each draft verification report will first be subjected to review by the respective EMS vendor, then revised and subjected to a review by EPA and other peer reviewers. The peer review comments will be addressed in further revisions of the report, and the peer review comments and responses will be tabulated to document the peer review process. The reporting and review process will be conducted according to the requirements of the ETV/AMS Center QMP.[2]

B2   SAMPLING METHOD REQUIREMENTS

The collection of reference samples will be conducted as described above (Section B1.1.1) by ARCADIS, under subcontract to Battelle, according to the requirements of Method 23.[1] Method 23 is the standard sampling method for dioxins from municipal waste combustors. The method uses sampling trains that consist of a heated probe, heated box containing a cyclone and a filter, water-cooled condenser, water-cooled XAD-2 resin 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. During the verification test, temperatures will be 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 will be conducted at the beginning and end of each sample run to ensure integrity of the sampling train. Prior to sampling, all glassware, probe, glass wool and aluminum foil will be cleaned following the Method 23 cleaning procedure, and the XAD traps will be spiked with carbon-13 labeled dioxin surrogate standards according to Method 23 to assess the efficiency of sample recovery from the sampling train. Sampling will be conducted at a sampling rate of approximately 0.75 cubic feet per minute (CFM), based on isokineticity between sampling nozzle flow and flow from the source. Section B5 describes the QA/QC requirements of Method 23.

The preparation of calibration and QC samples, and the analysis of samples for dioxins will be carried out according to Method 23 as described in Section B5. In addition, independent audits of sampling procedures will be carried out by Battelle as part of the technical systems audit procedure (Section C1.2) and the performance evaluation audit procedure (Section C1.1).

B3   SAMPLE HANDLING AND CUSTODY REQUIREMENTS

Following completion of each Method 23 run, each sampling train will be recovered in a clean area, and the cleanup procedure will begin as soon as the probe is 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 will be sealed with aluminum foil or glass caps.

The sample fractions from each train shall include the following:

> ➢ Filter

➢ XAD-2 Resin Cartridge

➢ Front-half acetone/dichloromethane rinse collection jar

➢ Front-half toluene rinse collection jar

➢ Back-half acetone/dichloromethane rinse collection jar

➢ Back-half toluene rinse collection jar.

The filter will be recovered and placed in a Petri dish that is sealed with Teflon tape. The probe and front half of the filter housing will be rinsed with acetone followed by dichloromethane. The solvents will be collected in a single 250 mL amber jar. This fraction will be designated as the acetone/dichloromethane front-half rinse sample. The probe and filter housing will then be rinsed with toluene. The toluene will be collected in a separate 250 mL amber jar. This sample will be designated as the toluene front-half rinse sample. The collection of the rinses in separate bottles is a modification to Method 23.

The XAD-2 cartridges will be kept refrigerated prior to use and during transport to the facility to prevent evaporation of the pre-sampling surrogate standards. After sampling, the XAD-2 resin cartridge from each train shall be capped at both ends and wrapped in aluminum foil during transport. This fraction of the sampling train will be designated as the XAD-2 fraction. As with all sample fractions, the XAD-2 fractions will remain refrigerated during storage and transport. The back half of the filter housing, glass connection and condenser will be rinsed with acetone followed by dichloromethane. The solvents will be collected in a single 250 mL amber jar. This fraction will be designated as the acetone/dichloromethane back-half rinse sample. This glassware will then be rinsed with toluene and the solvent will be collected in a separate 250 mL amber jar. This fraction will be designated as the toluene back-half rinse sample. The solvent rinse jars shall be capped with Teflon lined caps and sealed with Teflon tape to prevent leakage and evaporation during transport. The recovered samples will be uniquely identified for each test run and stored in a refrigerated space before they are sent for analysis. The samples shall be refrigerated during transport to the analytical laboratory.

All reference samples will be in the custody of ARCADIS from sample collection through sample recovery and in the custody of EPA staff for analysis. Recovered samples will be carried by ARCADIS staff to the EPA laboratory for analysis. Sample custody will be documented throughout collection, recovery, and analysis of the reference samples, using standard forms used by ARCADIS for this purpose. Each chain-of-custody form will be signed by the person relinquishing samples once that person has verified that the chain-of-custody form is accurate. Upon receipt at the laboratory, chain-of-custody forms will be signed by the person receiving the samples once that person has verified that all samples identified on the chain-of-custody forms are present in the shipping container. Any discrepancies will be noted on the form and the sample receiver will immediately contact the ARCADIS technical lead to report missing, broken, or compromised samples. Copies of all chain-of-custody forms will be delivered to the Verification Testing Coordinator upon request, and maintained with the test records.

B4   ANALYTICAL METHOD REQUIREMENTS

Analysis of the reference samples for dioxins will be conducted at the EPA RTP Campus, using a modified version of Method 23. The modifications to Method 23 that will be followed for this verification test include:

- ➤ Analysis will be completed by high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS). (The expected resolution for the LRMS is approximately 400, rather than 10,000 as stated for high resolution mass spectrometry.)
- ➤ Mass locking will not be used with LRMS.

The extraction and cleanup procedures for the target compounds of interest shall follow Method 23, with the exception that:

> ➢ The front and back halves of the reference samples will be extracted and analyzed together rather than separately.

> ➢ The internal, surrogate, and recovery standards that are used in the modified method include several that are not included in the standard method. A list of these standards is presented in Appendix A.

ARCADIS will coordinate the analysis of the reference method samples, which will be conducted by EPA staff at the EPA RTP facility. EPA staff will be responsible for ensuring that the calibration of the analytical instrumentation and the analysis of the samples are conducted according to the requirements of the modified Method 23, and for ensuring that the appropriate QA/QC activities are conducted according to the method (see Section B5). ARCADIS will ensure that the calibration records for any instrumentation used are maintained and will be responsible for providing Battelle with documentation on calibration and quality control of the reference analyses, upon request.

B5   QUALITY CONTROL REQUIREMENTS

As described in Section A7, reference dioxin sampling will be carried out using Method 23,[1] and will be subject to the data quality criteria of that method. The analysis of the reference samples will be conducted according to Method 23, including the modifications described in Section B4, and will be subject to the data quality criteria of that method. Table B3 summarizes the quality control requirements of those two methods. If the sampling or analytical performance strays outside the required tolerances, the relevant QC checks will be conducted again or the relevant QC samples will be prepared again and reanalyzed. If performance problems persist, the reference instrument will be recalibrated, and/or affected samples will be reanalyzed. Reference sample results not meeting the requirement will be excluded from comparison to the dioxin EMS results.

Table B3. QC Checks for Method 23

Measured Parameter	QC Check	Required Performance
Overall cleanup and analysis method efficiency	Internal standard recovery	Recovery: 40 to 130% for tetra- through hexachlorinated compounds; and 25 to 130% for hepta- and octachlorinated compounds
Sampling train integrity	Leak check	Leak rate of less than 0.02 ft^3/min
Sample train collection efficiency	Surrogate standard recovery	Goal of 70 to 130% recovery, otherwise correction is necessary
GC column performance	Performance check samples	Retention times within 10 seconds of expected retention times
Reagent solution contamination	Solution blanks	Blank <10% of sample or <10 x LOD, subtract blank from samples; if blank >10% of sample, data must be flagged
Sampling media contamination	Field blanks	if blank >30% of sample, data must be flagged
Precision of Method 23 sampling trains	Duplicate reference samples collected at each end of sampling duct	If concentrations do not agree within ±30% the data must be flagged and samples treated independently

B6   INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

The equipment used for the reference sampling and analysis will be tested, inspected, and maintained so as to meet the performance requirements established in Method 23. System preventive maintenance will be performed prior to the start of each test as needed. All major components will be checked to ensure operability and repaired when required. Laboratory equipment maintenance is conducted as recommended by the manufacturer on an as-needed basis. Daily calibrations of the CEMs will be conducted to ensure continued reliable operation and provide the operator warnings of abnormal operation.

The EPA Metrology Laboratory, prior to the start of the sampling program, will calibrate field-sampling equipment, such as Method 5 meter boxes for volumetric flow rates. Any leaks that

have developed will be repaired, parts will be lubricated as recommended by the manufacturer, and manometers will be filled and checked for leaks. Replacement parts, including fuses, pumps, spare tubing, compression fittings, etc., are maintained in the laboratory to minimize downtime. Equipment manufacturers and overnight delivery services will be utilized for repair parts in emergency situations.

If Battelle or ARCADIS staff operate and maintain the dioxin EMSs undergoing testing, those activities will be done as directed by the vendor. Otherwise, operation and maintenance of the EMSs will be the responsibility of the EMS vendors.

B7   INSTRUMENT CALIBRATION AND FREQUENCY

B7.1   Sampling Equipment Calibration

The instrumentation used for the reference sample collection and analysis will be calibrated per the requirements stated in the EPA certified methods. EPA methods require that a laboratory record be maintained of all calibrations. The calibration requirements of Method 23 include the following minimal calibration activities:

- ➢ Standard Pitot tube will be inspected and cleaned before each Method 23 test run.

- ➢ The volume metering system will be calibrated within six months of use during the verification test using a wet-test meter, as permitted in the Method.

- ➢ All thermocouples and dial thermometers will be calibrated within six months of use during the verification test. Thermometric fixed points (i.e. ice bath and boiling water) are adequate standards for this task.

- ➢ The portion of the volume metering system from the pump to the orifice meter will be leak checked following each test, using the procedure described in EPA Method 5, Section 8.4.

➢ Barometers will be calibrated within six months of use during the verification test by reference to a mercury barometer or a local National Weather Service station. Corrections will be made at a rate of -0.1 inches Hg per 100 feet of elevation above sea level.

Additionally, to ensure the accurate measurement of the flue gas conditions,

➢ The two self-contained bench-scale CEM systems at the SMPB will be calibrated at the start of each sampling day, and verified at the end of each sampling day to correct for possible sample drift and bias.

B7.2   Analytical Instrumentation Calibration

Prior to sample analysis, a calibration of the analytical instrumentation must be conducted according to Section 6 of Method 23. Also, a daily performance check must be conducted daily according to Section 6.1.2 of Method 23.

B7.3   Dioxin EMS Calibration

The dioxin EMSs undergoing testing will be calibrated initially by the respective EMS vendors at the time of installation at the host facility. In the event that recalibration is necessary, that recalibration will be carried out by the EMS vendor, or by Battelle staff under the direction of the vendor. All calibrations performed will be documented by Battelle or host facility staff in the project record book dedicated to the respective EMS.

B8   INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

All materials, supplies, and consumables will be ordered by the Verification Test Coordinator or designee. Where possible, Battelle will rely on sources of materials and consumables that have been used previously as part of ETV verification testing without problems. Battelle will also rely on previous experience or recommendations from EPA advisors, ARCADIS staff, or EMS vendors. Upon receipt of any supplies or consumables, the Verification Test Coordinator or his designee will visually inspect and ensure that the materials received are those that were ordered and that there are no visual signs of damage that could compromise the suitability of the materials. If damaged or inappropriate goods are received they will be returned or disposed of and arrangements will be made to receive replacement materials. Certificates of analysis (COA) or other documentation of analytical purity will be checked for all gases, reagents, and standards to ensure suitability for this verification test. Unsuitable materials will be returned or disposed of and arrangements for the receipt of replacement materials will be made.

B9   NON-DIRECT MEASUREMENTS

No non-direct measurements will be used during this verification test.

B10   DATA MANAGEMENT

Various types of data will be acquired and recorded electronically or manually by Battelle, vendor, and ARCADIS staff during this verification test. All data will be recorded in permanent ink. Corrections to records will be made by drawing a single line through the entry to be corrected and providing a simple explanation for the correction, along with a date and the initials of the person making the correction. Table B4 summarizes the types of data to be recorded. All maintenance activities, repairs, calibrations, and operator observations relevant to the operation of the dioxin EMSs will be documented by Battelle or ARCADIS staff in laboratory record

Table B4. Summary of Data Recording Process

Data to Be Recorded	Where Recorded	How Often Recorded	By Whom	Disposition of Data
Dates, times, and details of test events, EMS maintenance, down time, etc.	ETV test notebooks	Start/end of test procedure, and at each change of a test parameter or change of EMS status	Battelle and ARCADIS	Used to organize/check test results; manually incorporated in data spreadsheets as necessary
EMS calibration information	ETV test notebooks, or electronically	At EMS calibration or re-calibration	Vendor, Battelle, and ARCADIS	Incorporated in verification report as necessary
EMS readings	Recorded electronically by each monitor and then downloaded to computer at the close of each day.	Recorded continuously, or as determined by each EMS.	EMS vendor, for transfer to Battelle	Converted to spreadsheet for statistical analysis and comparisons
Integrated EMS measurement results	Electronically from analytical method	Every sample analysis	Analytical laboratory	Converted to spreadsheets for calculation of flue gas dioxin concentrations, and statistical analysis and comparisons
Reference method procedures, calibrations, QA, etc.	Laboratory record books, or data recording forms	Throughout sampling and analysis processes	ARCADIS	Retained as documentation of reference method performance
Reference method analysis results	Electronically from analytical method	Every sample analysis	ARCADIS	Converted to spreadsheets for calculation of flue gas dioxin concentrations, and statistical analysis and comparisons

books. Results from the reference method will be compiled by ARCADIS staff in electronic format, and submitted to Battelle in the form of a sampling and analysis report at the conclusion of reference dioxin analyses.

Records received by or generated by any Battelle or ARCADIS staff during the verification test will be reviewed by a Battelle staff member within two weeks of receipt or generation, respectively, before the records are used to calculate, evaluate, or report verification results. If a

Battelle staff member generated the record, this review will be performed by a Battelle technical staff member involved in the verification test, but not the staff member who originally received or generated the record. The review will be documented by the person performing the review by adding his/her initials and date to the hard copy of the record being reviewed. In addition, any calculations performed by Battelle or ARCADIS staff will be spot-checked by Battelle technical staff to ensure that calculations are performed correctly. Calculations to be checked include any statistical calculations described in this test/QA plan. The data obtained from this verification test will be compiled and reported independently for each dioxin EMS. Results for EMSs from different vendors will not be compared with each other.

Among the QA activities conducted by Battelle QA staff will be an audit of data quality. This audit will consist of a review by the Battelle Quality Manager of at least 10% of the test data. During the course of any such audit, the Battelle Quality Manager will inform the technical staff of any findings and any immediate corrective action that should be taken. If serious data quality problems exist, the Battelle Quality Manager will inform the AMS Center Manager who is authorized to stop work. Once the assessment report has been prepared, the Verification Test Coordinator will ensure that a response is provided for each adverse finding or potential problem, and will implement any necessary follow-up corrective action. The Battelle Quality Manager will ensure that follow-up corrective action has been taken.

SECTION C
ASSESSMENT AND OVERSIGHT

C1   ASSESSMENTS AND RESPONSE ACTIONS

Every effort will be made in this verification test to anticipate and resolve potential problems before the quality of performance is compromised. One of the major objectives of this test/QA plan is to establish mechanisms necessary to ensure this. Internal quality control measures described in this test/QA plan, which is peer reviewed by a panel of outside experts, implemented by the technical staff and monitored by the Verification Test Coordinator, will give information on data quality on a day-to-day basis. The responsibility for interpreting the results of these checks and resolving any potential problems resides with the Verification Test Coordinator. Technical staff have the responsibility to identify problems that could affect data quality or the ability to use the data. Any problems that are identified will be reported to the Verification Test Coordinator, who will work with the Battelle Quality Manager to resolve any issues. Action will be taken to control the problem, identify a solution to the problem, and minimize losses and correct data, where possible. Independent of any EPA QA activities, Battelle will be responsible for ensuring that the following audits are conducted as part of this verification test.

C1.1   Performance Evaluation Audit

A Performance Evaluation (PE) audit will be conducted to assess the quality of the critical measurements associated with the reference sampling and analysis methods. In the PE audit, critical measurements associated with the reference methods will be checked by comparison with an independent instrument, or an independent NIST-traceable standard. Table C1 shows the critical measurements to be audited, with the audit procedures and acceptance criteria for the audit comparisons. If the PE audit results do not meet the acceptance criteria shown, they will be repeated. If the outlying results persist, a change in reference instrument and a repeat of the PE

Table C1. Methods and Acceptance Criteria for PE Audit Measurements

Critical Measurement	PE Audit Method	Acceptance Criteria
Method 23 gas sample flow rate	Compare to independent flow measurement device	±5%
Method 23 stack gas temperature	Compare to independent temperature measurement device	±2% absolute temperature
Barometric pressure	Compare to independent pressure gauge	±1% absolute pressure
Dioxin internal standard recovery	Method spike with an independent dioxin standard	40 to 130% for tetra- through hexachlorinated compounds; and 25 to 130% for hepta- and octachlorinated compounds
Dioxin surrogate standard recovery	Field spike with an independent dioxin standard	70 to 130% recovery

audit may be considered, and data will be flagged until the PE audit results are acceptable. This audit will be performed once during the verification test, and will be the responsibility of the Verification Test Coordinator or his designee.

The PE audit of the surrogate standard recovery will be performed by spiking one blank Method 23 train with a NIST-traceable dioxin solution, provided by Battelle. The spiked train will not be used to collect a flue gas sample but will be recovered and analyzed in the same manner as for all other Method 23 trains, and the analytical results will be compared to the spike amount to assess recovery. The target criteria for this PE audit are 40-130% recovery of the surrogate standards for the tetra-through hexachlorinated compounds, and 25-130% for the hepta- and octa-chlorinated compounds. If these criteria are not met, the data will be flagged and noted in the verification report.

The PE audit of the internal standard recovery will be performed by spiking one blank XAD-cartridge with a NIST-traceable dioxin internal standard solution provided by Battelle rather than the internal standard solution typically used by the laboratory. This spiked cartridge will be extracted and analyzed in the same manner as for all the other cartridges. The target criterion for

this PE audit is 70-130% recovery of the internal standards. If this criterion is not met, the data will be flagged and congener-specific correction factors will be applied to account for material loss (or gain).

C1.2 Technical Systems Audits

The Battelle Quality Manager will perform a technical systems audit (TSA) at least once during this verification test. The purpose of this audit is to ensure that the verification test is being performed in accordance with the AMS Center QMP,[2] this test/QA plan, published reference methods, and any SOPs used by the test facility. In this audit, the Battelle Quality Manager, or designee, may review the reference methods used, compare actual test procedures to those specified or referenced in this plan, and review data acquisition and handling procedures. In the TSA, the Battelle Quality Manager will tour the test site and EMS locations; observe the Method 23 sampling and sample recovery; inspect documentation of reference sample chain of custody; and review laboratory record books. He will also check gas standard certifications and EMS data acquisition procedures, and may confer with the EMS vendors and ARCADIS testing staff. A TSA report will be prepared, including a statement of findings and the actions taken to address any adverse findings. The EPA AMS Center Quality Manager will receive a copy of Battelle's TSA report. At EPA's discretion, EPA QA staff may also conduct an independent on-site TSA during the verification test. The TSA findings will be communicated to technical staff at the time of the audit and documented in a TSA report.

C1.3 Data Quality Audits

The Battelle Quality Manager, or his designee, will audit at least 10% of the verification data acquired in the verification test. The Battelle Quality Manager, or his designee, will trace the data from initial acquisition, through reduction and statistical comparisons, to final reporting. All calculations performed on the data undergoing the audit will be checked.

C1.4 QA/QC Reporting

Each assessment and audit will be documented in accordance with Section 3.3.4 of the AMS Center QMP.[2] The results of the TSA will be submitted to EPA. Assessment reports will include the following:

- C Identification of any adverse findings or potential problems
- C Response to adverse findings or potential problems
- C Recommendations for resolving problems
- C Confirmation that solutions have been implemented and are effective
- C Citation of any noteworthy practices that may be of use to others.

C2   REPORTS TO MANAGEMENT

The Battelle Quality Manager, during the course of any assessment or audit, will identify to the technical staff performing experimental activities any immediate corrective action that should be taken. If serious quality problems exist, the Battelle Quality Manager will notify the AMS Center Manager, who is authorized to stop work. Once the assessment report has been prepared, the Verification Test Coordinator will ensure that a response is provided for each adverse finding or potential problem and will implement any necessary follow-up corrective action. The Battelle Quality Manager will ensure that follow-up corrective action has been taken. The test/QA plan and final report are reviewed by EPA AMS Center quality assurance staff and the EPA AMS Center program management staff. Upon final review and approval, both documents will then be posted on the ETV website (www.epa.gov/etv).

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SECTION D

DATA VALIDATION AND USABILITY

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D1   DATA REVIEW, VERIFICATION, AND VALIDATION REQUIREMENTS

The key data review and data verification requirements for this test are stated in Section B10 of this test/QA plan. In general, the data review requirements specify that data generated during this test will be reviewed by a Battelle technical staff member within two weeks of generation of the data. The reviewer will be familiar with the technical aspects of the verification test but will not be the person who generated the data. This process will serve both as the data review and the data verification, and will ensure that the data have been recorded, transmitted and processed properly. Furthermore, this process will ensure that the EMS data and reference method data were collected under appropriate testing conditions and that the reference sample data meet the specifications of Method 23.

The data validation requirements for this test involve an assessment of the quality of the data relative to the DQIs and audit acceptance criteria specified for this test. The DQIs listed in Section B5 will be used to validate the quality of the data. The QA audits described within Section C of this document, including the performance evaluation audit and the audit of data quality, are also designed to validate the quality of the data.

D2   VERIFICATION AND VALIDATION METHODS

Data verification is conducted as part of the data review as described in Section B10 of this test/QA plan. A visual inspection of handwritten data will be conducted to ensure that all entries were properly recorded or transcribed, and that any erroneous entries were properly noted (i.e., single line through the entry, with an error code and the initials of the recorder and date of entry). Electronic data from the CEMs, EMSs, and other instruments used during the test will be

inspected to ensure proper transfer from the datalogging system. All calculations used to transform the data will be reviewed to ensure the accuracy and the appropriateness of the calculations. Calculations performed manually will be reviewed and repeated using a handheld calculator or commercial software (e.g., Excel). Calculations performed using standard commercial office software (e.g., Excel) will be reviewed by inspection of the equations used for the calculations and verification of selected calculations by handheld calculator. Calculations performed using specialized commercial software (i.e., for analytical instrumentation) will be reviewed by inspection and, when feasible, verified by handheld calculator, or standard commercial office software.

To ensure that the data generated from this test meet the goals of the test, a number of data validation procedures will be performed. Section C of this test/QA plan provides a description of the validation safeguards employed for this verification test. Data validation efforts include the completion of QC activities, and the performance of TSA and PE audits as described in Section C. The data from this test will be evaluated relative to the measurement DQIs described in Section B5, and the PE audit acceptance criteria given in Section C1.1 of this test/QA plan. Data failing to meet these criteria will be flagged in the data set and not used for evaluation of the EMS, unless these deviations are accompanied by descriptions of their potential impacts on the data quality.

An audit of data quality will be conducted by the Battelle Quality Manager to ensure that data review, verification, and validation procedures were completed, and to assure the overall quality of the data.

D3   RECONCILIATION WITH USER REQUIREMENTS

This purpose of this verification test is to evaluate the performance of commercial dioxin EMSs. In part, this evaluation will include comparisons of results from the EMSs to the results from reference samples generated from a well-established EPA method for sample collection, and a

second well-established EPA method for sample analysis. To meet the requirements of the user community, the reference data collected during this verification test should meet the QA requirements of the reference methods. Additional performance data will be collected by testing personnel regarding operational characteristics of the EMSs. To meet the requirements of the user community, these data should include thorough documentation of the performance of the EMSs during the verification test. The data review, verification, and validation procedures described above will assure that data meeting these requirements is accurately presented in the verification reports generated from this test, and will assure that data not meeting these requirements will be appropriately flagged and discussed in the verification reports.

This test/QA plan and the resulting ETV verification report(s) will be subjected to review by the EMS vendors, the host facility, EPA, and expert peer reviewers. The reviews of this test/QA plan will assure that this verification test and the resulting report(s) meet the needs of potential users and permitters of dioxin EMSs.

SECTION E

REFERENCES

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

3. Environmental Technology Verification Program Quality Management Plan, EPA/600/R-03/021, U.S. Environmental Protection Agency, Cincinnati, Ohio, December 2002

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.

APPENDIX A

Modified Method 23 Spiking Scheme

Modified Method 23 Spiking Scheme

Internal Standards   Pre Extraction Spike

$^{13}C_{12}$-2-MCDF
$^{13}C_{12}$-2-MCDD
$^{13}C_{12}$-2,4-DCDF
$^{13}C_{12}$-2,7-DCDD
$^{13}C_{12}$-2,4,8-TrCDF
$^{13}C_{12}$-2,3,7,8-TeCDF
$^{13}C_{12}$-2,3,7,8-TeCDD
$^{13}C_{12}$-1,2,3,7,8-PCDF
$^{13}C_{12}$-1,2,3,7,8-PCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
$^{13}C_{12}$-1,2,3,4,6,7,8,9-OCDD

Surrogate Standards   Pre-Sampling Spike on the XAD

$^{13}C_{12}$-2,8-DCDF
$^{13}C_{12}$-2,3-DCDD
$^{13}C_{12}$-2,3,7-TrCDD
$^{37}Cl_{4}$-2,3,7,8-TeCDD
$^{13}C_{12}$-2,3,4,7,8-PCDF
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF

Recovery Standards   Pre-Analysis Spike   (Spiked after Clean-up)

$^{13}C_{12}$-1,2,3,4-TeCDD
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD