Battelle
. . . Putting Technology To Work

Environmental Technology Verification Program

Advanced Monitoring Systems Center

Generic Protocol for Pilot-Scale Verification of Continuous Emission Monitors for Mercury

GENERIC PROTOCOL

FOR

PILOT-SCALE VERIFICATION OF CONTINUOUS EMISSION MONITORS FOR MERCURY

August 2002

Prepared by

Battelle
505 King Avenue
Columbus, OH 43201-2693

TABLE OF CONTENTS

Page

TABLE OF CONTENTS (Continued)

Page

List of Figures

TABLE OF CONTENTS (Continued)

Page

List of Tables

ACRONYMS

ACS	American Chemical Society
AMS	Advanced Monitoring Systems
ASAT	Atmospheric Science and Applied Technology
CEM	continuous emission monitor
Cl_2	chlorine
CO	carbon monoxide
CO_2	carbon dioxide
CVAAS	cold vapor atomic absorption spectroscopy
CVAFS	cold vapor atomic fluorescence spectroscopy
EM	elemental mercury
EPA	United States Environmental Protection Agency
ETV	Environmental Technology Verification
HCl	hydrogen chloride
Hg	mercury
Hg^o	mercury vapor phase
l	liter
ml	milliliter
NIST	National Institute of Standards and Technology
NO	nitric oxide
NO_x	nitrogen oxides
O_2	oxygen
OH	Ontario Hydro
OM	oxidized mercury
PE	performance evaluation
PM	particulate mercury
ppb	parts per billion

ACRONYMS (Continued)

ppm	parts per million
QA	quality assurance
QC	quality control
QMP	Quality Management Plan
RKIS	Rotary Kiln Incinerator Simulator
SDAS	Statistics and Data Analysis Systems
SO_2	sulfur dioxide
TM	total mercury
TSA	technical systems audit
TVM	total vapor-phase mercury

1 INTRODUCTION

1.1 Test Description

This test protocol provides generic procedures for implementing a verification test of continuous emission monitors (CEMs) used to measure total and chemically speciated mercury (Hg) in source emissions. Verification tests are conducted under the auspices of the U.S. Environmental Protection Agency (EPA) through its Environmental Technology Verification (ETV) program. The purpose of the ETV program is to provide objective and quality-assured performance data on environmental technologies, so that users, developers, regulators, and consultants can make informed decisions about this technology.

The verification tests are performed by Battelle, of Columbus, Ohio, which is EPA's partner for the ETV Advanced Monitoring Systems (AMS) Center. The scope of the AMS Center covers verification of monitoring methods for contaminants and natural species in air, water, and soil. In performing verification tests, Battelle follows the procedures specified in this protocol and complies with quality requirements in the "Quality Management Plan for the ETV Advanced Monitoring Systems Center" (QMP).[1]

1.2 Test Objective

The purpose of verification tests of commercial mercury CEMs is to evaluate their performance by comparing them to a reference method for measuring Hg and by challenges with mercury standard gases and interferences, under controlled conditions in a pilot-scale combustion facility. A subsequent test, based on a separate protocol, may be conducted to assess performance at a full-scale facility.

1.3 Roles and Responsibilities

The verification test is performed by Battelle in cooperation with EPA and the vendors whose CEMs will be verified. The chart in Figure 1 shows the organization of responsibilities for Battelle, the vendor companies, and EPA. Specific responsibilities are detailed below.

1.3.1 Battelle

The AMS Center Verification Test Coordinator has the overall responsibility for ensuring that the technical, schedule, and cost goals established for the verification test are met. The Verification Test Coordinator shall

- Coordinate Battelle, EPA, contractor, and vendor staff to conduct the verification test
- Ensure that Battelle/EPA/contractor/vendor team perform the verification test in accordance with all quality procedures specified in the test/quality assurance (QA) plan and the QMP
- Have overall responsibility for ensuring that this test/QA plan is followed
- Prepare a draft test/QA plan, verification reports, and verification statements
- Revise the draft test/QA plan, verification reports, and verification statements in response to reviewers' comments
- Coordinate distribution of the final test/QA plan, verification reports, and statements
- 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
- Establish a budget for the verification test and monitor staff effort to ensure that budget is not exceeded
- Ensure that confidentiality of vendor information is maintained
- Ensure that all quality procedures are followed.

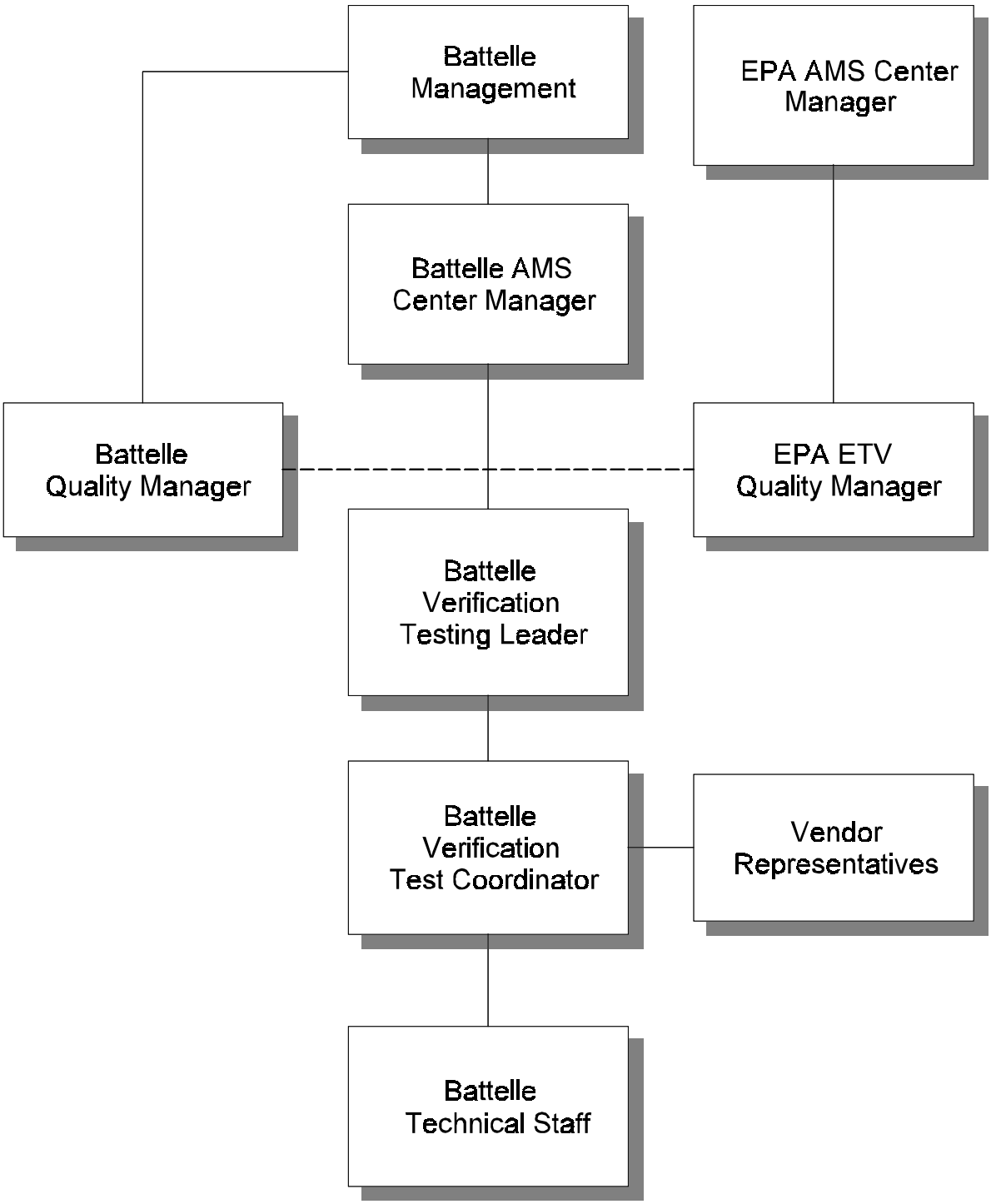

Figure 1. Organization Chart for the Mercury CEM Verification Test

The Verification Testing Leader for the AMS Center provides technical guidance and oversee the various stages of the verification test. The Verification Testing Leader shall

- Support the Verification Test Coordinator in preparing the test/QA plan and organizing the test
- Review the draft test/QA plan
- Review the draft verification reports and statements
- Ensure that vendor confidentiality is maintained.

The Battelle AMS Center Manager shall

- Review the draft test/QA plan
- Review the draft verification reports and statements
- Ensure that necessary Battelle resources, including staff and facilities, are committed to the verification test
- Ensure that vendor confidentiality is maintained
- Support Verification Test Coordinator in responding to any issues raised in assessment reports and audits
- Maintain communication with EPA's Center and ETV Quality Managers.

The Battelle Quality Manager for this verification test shall

- Review the draft test/QA plan
- Maintain communication with EPA's Quality Manager for the AMS Center
- Conduct a TSA once during the verification test
- Review results of performance evaluation audit(s) specified in the test/QA plan
- Audit at least 10% of the verification data

- Prepare and distribute an assessment report for each audit
- Verify implementation of any necessary corrective action
- Issue a stop work order if self-audits indicate that data quality is being compromised; notify Battelle's AMS Center Manager if a stop work order is issued
- Provide a summary of the audit activities and results for the verification reports
- Review the draft verification reports and statements
- Ensure that all quality procedures specified in this test/QA plan and in the QMP[(1)] are followed.

Staff statisticians shall provide statistics and data analysis support. In particular, statistical staff shall

- Contribute to planning statistical treatment of the CEM data
- Perform statistical calculations specified in the test/QA plan on the analyzer data
- Provide results of statistical calculations and associated discussion for the verification reports
- Support the Verification Test Coordinator in responding to any issues raised in assessment reports and audits related to statistics and data reduction.

Battelle Atmospheric Science and Applied Technology (ASAT) staff shall support the Verification Test Coordinator in planning and conducting the verification test. ASAT staff shall

- Assist in planning for the test and making arrangements for installing the CEMs
- Assist vendors and test facility staff as needed during the CEM installation and verification testing
- Assure that test procedures and data acquisition are conducted according to the test/QA plan.

1.3.2 Vendors

Vendor representatives shall

- Review the draft test/QA plan
- Approve the final test/QA plan
- Participate in required safety training at the test facility before installation of their CEMs
- Attend a pre-study site visit to review facility requirements for testing
- Provide a mercury CEM for the duration of the verification test
- Commit a trained technical person to operate, maintain, and repair the CEMs throughout the verification test
- Participate in verification testing, including providing data acquisition for their mercury CEMs
- Provide to Battelle staff the data from the CEMs at the conclusion of each test day
- Review their respective draft verification reports and verification statements.

1.3.3 EPA

EPA's responsibilities in the AMS Center are based on the requirements stated in the "Environmental Technology Verification Program Quality and Management Plan for the Pilot Period (1995-2000)"[(2)] or the most current update of this document. The roles of specific EPA staff are as follows:

EPA's ETV Quality Manager shall

- Review the draft test/QA plan
- Perform, at his/her option, one external TSA during the verification test

- Notify the Battelle AMS Center Quality Manager to facilitate a stop work order if an external audit indicates that data quality is being compromised
- Prepare and distribute an assessment report summarizing the results of an external audit, if performed
- Review the draft verification reports and statements.

The EPA AMS Center Manager shall

- Review the draft test/QA plan
- Approve the final test/QA plan
- Review the draft verification reports and statements
- Oversee the EPA review process on the draft verification test/QA plan, reports, and statements
- Coordinate the submission of verification reports and statements for final EPA approval.

This verification test may be conducted in collaboration with non-Battelle staff operating the pilot-scale facility. The operator's responsibilities are to

- Coordinate the operation of the pilot-scale facility for the purposes of ETV testing
- Conduct pre-verification testing to document the capabilities of the pilot-scale facility and reference methods
- Coordinate the installation of vendor equipment at the pilot-scale facility
- Communicate needs for safety and other training of staff working at the pilot-scale facility
- Contribute to the development of the draft test/QA plan
- Review the draft test/QA plan
- Provide input for the verification test reports

- Provide input in responding to any issues raised in assessment reports and audits related to pilot-scale facility operations
- Review draft verification reports and verification statements.

1.3.4 Contractor

The contractor operating the pilot-scale facility may perform some duties under contract with EPA and additional duties related to the verification test under a subcontract with Battelle. The contractor's responsibilities may include

For EPA:

- Assemble trained technical staff to operate the pilot-scale facility
- Ensure that the facility is fully functional prior to the times/dates needed in the verification test
- Oversee technical staff in facility operation during the verification test
- Ensure that operating conditions and procedures for the pilot-scale facility are recorded during the verification test
- Review and approve all data and records related to facility operation.

For Battelle:

- Review the draft test/QA plan
- Adhere to the quality requirements in this test/QA plan and in the QMP
- Assemble trained technical staff to conduct reference method sampling for the verification test
- Contract for and oversee laboratory analysis of the reference method samples
- Report reference method analytical and QA results to Battelle in an agreed-upon format

- Provide input on facility operating conditions and procedures for the verification test report
- Support the Verification Test Coordinator in responding to any issues raised in assessment reports and audits related to facility operation.

2 APPLICABILITY

2.1 Subject

This generic protocol is applicable to the verification testing of commercial CEMs for determining total and/or chemically speciated Hg in combustion source emissions. Total Hg is the sum of Hg in all phases and chemical forms in the combustion gas, including elemental mercury (Hg^o), oxidized mercury (typically mercuric chloride [($HgCl_2$), and/or mercuric oxide (HgO) vapors)], and particulate-phase mercury. Most commercial Hg CEMs do not measure the particulate phase Hg; instead they filter out particulate matter and measure the total of the vapor-phase Hg species. This approach is taken because, at least for electrical-generating facilities, recent stack test results indicate that generally the great majority of emitted Hg is in the vapor phase.[3] Commercial CEMs may provide chemical speciation data, i.e., the oxidized and elemental fractions of the Hg vapor species are reported separately. This separation is usually accomplished by a difference measurement in which oxidized Hg is chemically reduced or thermally decomposed to elemental mercury for detection.

The commercial mercury CEMs also use a variety of final analytical approaches to detect Hg. Cold vapor atomic absorption spectroscopy (CVAAS), cold vapor atomic fluorescence spectroscopy (CVAFS), and differential optical absorption spectroscopy are all used, but can detect only elemental Hg, and so require the speciation approaches outlined above to determine oxidized Hg. Atomic emission spectroscopy is used in one commercial CEM and has the advantage that, in principle, all forms of Hg, including particulate, are converted to elemental Hg and detected equally. This approach provides a true total Hg measurement, but does not provide any information on speciation.

The terminology to be used in this generic verification test protocol is as follows:

- Total mercury (TM)—the sum of all vapor and particulate Hg, whether elemental or oxidized
- Total vapor-phase mercury (TVM)—the sum of all vapor-phase Hg species, whether elemental or oxidized
- Elemental mercury (EM)—vapor-phase Hg°
- Oxidized mercury (OM)—the sum of vapor-phase non-elemental Hg, regardless of chemical species (e.g., $HgCl_2$, and others)
- Particulate mercury (PM)—Hg in the particulate phase.

The CEMs tested according to this protocol shall be verified for their measurement of any and all of the applicable Hg components listed above. For example, a monitor that determines TVM and EM, and by difference determines OM, will be verified for measuring all three components. In the United States, emission regulations on combustion sources are expected to address only total Hg. However, there are valuable non-regulatory uses of Hg speciation data; and, therefore, speciation capabilities of the CEMs will be verified.

Verification testing requires a basis for establishing the quantitative performance of the tested technologies. For the verification testing conducted under this protocol, the basis of comparison consists of a reference method of measurement, i.e. the Ontario Hydro (OH) method,[4] currently recognized as the most suitable procedure to determine oxidized and elemental Hg in source emissions. This method is specifically designed for use in environments containing high levels of sulfur dioxide (SO_2) and has shown agreement within about 10% for total Hg with EPA Method 101A, in trial runs at the pilot facility to be used for this verification[5] and in other sampling tests.[e.g., 6]

This generic test protocol calls for the use of a natural-gas-fired pilot-scale incineration facility as the test bed for the verification. Such a facility allows flexibility in simulating different sources of combustion flue gas, such as coal combustion or mixed waste incineration, by injecting constituents into the combustion zone. However, other combustion sources may also be used, provided they allow appropriate control of test conditions and Hg levels.

2.2 Scope

The overall objective of the verification test derived from this protocol is to provide quantitative verification of the performance of the Hg CEMs in realistic test conditions. Since Hg CEMs are a relatively new group of instruments, performance expectations and procedures to assess their performance are not fully established. EPA has published the draft performance specification document, PS-12,[7] a proposed description of how to assess the acceptability of a Hg CEM upon installation and thereafter. However, the draft PS-12 is patterned after performance specifications for CEMs for other pollutants, such as SO_2 and nitrogen oxides (NO_x); and, as a result, it includes requirements that are inappropriate or currently not feasible. For example, the draft PS-12 requires the CEM to measure both vapor and particulate phase Hg. As noted above, most current CEMs do not determine particulate-phase Hg. Also, the draft PS-12 requires absolute standards for both EM and OM (the latter in the form of $HgCl_2$). Although elemental Hg compressed gas standards are becoming commercially available, they have not yet been widely used. The stability of such standards appears to be good enough to assess instrument drift and precision,[e.g., 8] but their absolute quantitation may not be sufficient to assess instrument accuracy. Comparable standards for $HgCl_2$ do not yet exist. As a result of factors such as these, and because PS-12 is a draft document soon to be revised, it is not appropriate to adopt PS-12 procedures as the basis for this verification test. Instead, tests should be designed to evaluate CEM performance on key monitoring characteristics, while addressing some performance requirements raised in PS-12 as closely as possible.

The performance parameters that are addressed by this test protocol include:

- Relative accuracy
- Correlation with reference method
- Precision
- Calibration drift
- Zero drift
- Sampling system bias

- Interference response
- Response time.

Relative accuracy, correlation with the reference method, and precision (i.e., repeatability at stable test conditions) shall be assessed for whichever of the TM, EM, OM, and PM fractions are measured by the commercial CEM. Calibration and zero drift, response time, and sampling system bias shall be assessed for EM only, using commercial compressed gas standards of EM. Interference response shall be assessed in sampling the combustion facility flue gas, rather than in sampling diluted calibration gases, as called for in PS-12. Calibration error is not assessed in this test because of the absence of absolute standards.

It is beyond the scope of a verification test derived from this protocol to simulate the aging and exposures that may affect a CEM during routine long-term use. This protocol describes a verification test that evaluates the performance of new CEMs installed in a pilot-scale facility, over a relatively short test period, in the hands of skilled vendor staff. It must be noted that long-term performance may be different from that observed in the testing described here. However, the effort spent in installing and maintaining each CEM shall be documented, and the amount of time each CEM is operational over the verification test period shall be recorded to assess data completeness.

3 SITE DESCRIPTION

The verification test described in this protocol was conducted at the Rotary Kiln Incinerator Simulator (RKIS) at the EPA Incineration Research Laboratory in Research Triangle Park, North Carolina. While this protocol discusses, in detail, the facilities and capabilities of the RKIS, the protocol may be adapted for other test facilities. If another facility is used, care must be taken to make sure it meets the minimum requirements for this protocol. These include

- Multiple ports for isokinetic flue gas sampling
- Ability to measure O_2, CO_2, CO, SO_2, NO/NO_x, and hydrogen chloride (HCl)

- Ports for injecting interferents
- Ability to introduce Hg into flue gas at reproducible concentrations
- Ability to conduct OH reference method measurements and analyze resulting samples
- Ability to inject particulate into flame zone.

Through the remainder of this protocol, the RKIS is used as a specific test facility example. This section of the protocol describes the RKIS and the procedures for operating it for this test.

3.1 Test Facility

A schematic diagram of the RKIS is provided in Figure 2, and the RKIS design characteristics are provided in Table 1. The RKIS was modified in 1997 for a simultaneous test of eight multi-metal CEMs; Figure 2 and Table 1 reflect those modifications. The RKIS consists of a primary combustion chamber, a transition section, and a fired afterburner in the secondary combustion chamber. Both the kiln and afterburner are fitted with 73-kW (0.25-MMBtu/h) auxiliary fuel burners. Natural gas is the primary fuel, although liquid waste or fuel oil can also be fired. Typical firing rates are 29 to 88 kW (0.1 to 0.3 MMBtu/h) to each of the kiln sections and the afterburner.

Combustion flue gases exiting the afterburner are rapidly cooled to approximately 540°C (1,000°F) as they pass through a water-jacketed section of ductwork. Further cooling, to approximately 340°C (650°F) or less, is achieved by adding air through an air dilution damper just upstream of a 9.9-m (35-ft) long, 20.3-cm (8-in.) diameter duct that contains the sampling ports. Both the CEMs to be tested and the reference method measurements will use these sampling ports.

Access for isokinetic flue gas sampling is available at several locations in the duct noted above, via standard 3-inch (7.6-cm) and 4-in. (10.2-cm) diameter National Pipe Thread couplings. These sampling ports are located in straight horizontal and vertical runs of circular cross section, nominally 8-in. (20.3-cm) diameter, Schedule-10 stainless steel pipe. The sampling ports are configured as a ring of three ports, which includes a 10.2-cm (4-in.) diameter

Table 1. Design Characteristics of the RKIS

Characteristics of the Primary Combustion Chamber	
Length	1.83 m (6 ft)
Diameter, Outside	1.22 m (4 ft)
Diameter, Inside	Nominal 0.76 m (2.5 ft)
Chamber Volume	0.28 m^3 (9.9 ft^3)
Construction	0.64 cm (0.25 in) thick cold-rolled steel
Refractory	23 cm (9 in) thick high alumina castable refractory at maximum I.D. point
Rotation	Counterclockwise, 0.25 to 2 rpm
Solids Retention Time	Batch system—solids remain until physically removed
Burner	Custom burner based on IFRF design rated at 73 kW (0.25 MMBtu/h) with liquid feed capability
Primary Fuel	Natural gas
Feed System:	
Liquids	Fuel oil or liquid waste pumped into burner
Solids	Manual batch containers fed with ram rod
Temperature (max.)	1,100°C (2,000°F)
Characteristics of the Afterburner Chamber	
Length	3 m (10 ft)
Diameter, Outside	1.22 m (4 ft)
Diameter, Inside	0.61 m (2 ft)
Chamber Volume:	
Mixing Chamber	0.18 m^3 (6.3 ft^3)
Plug Flow Chamber	0.45 m^3 (16 ft^3)
Construction	0.64 cm (0.25 in) thick cold-rolled steel
Refractory	30 cm (12 in) thick high alumina castable refractory
Gas Residence Time	2 to 5 s depending on temperature and excess air
Burner	Custom burner based on IFRF design rated at 73 kW (0.25 MMBtu/h)
Primary Fuel	Natural gas
Temperature (max.)	1,100°C (2,000°F)

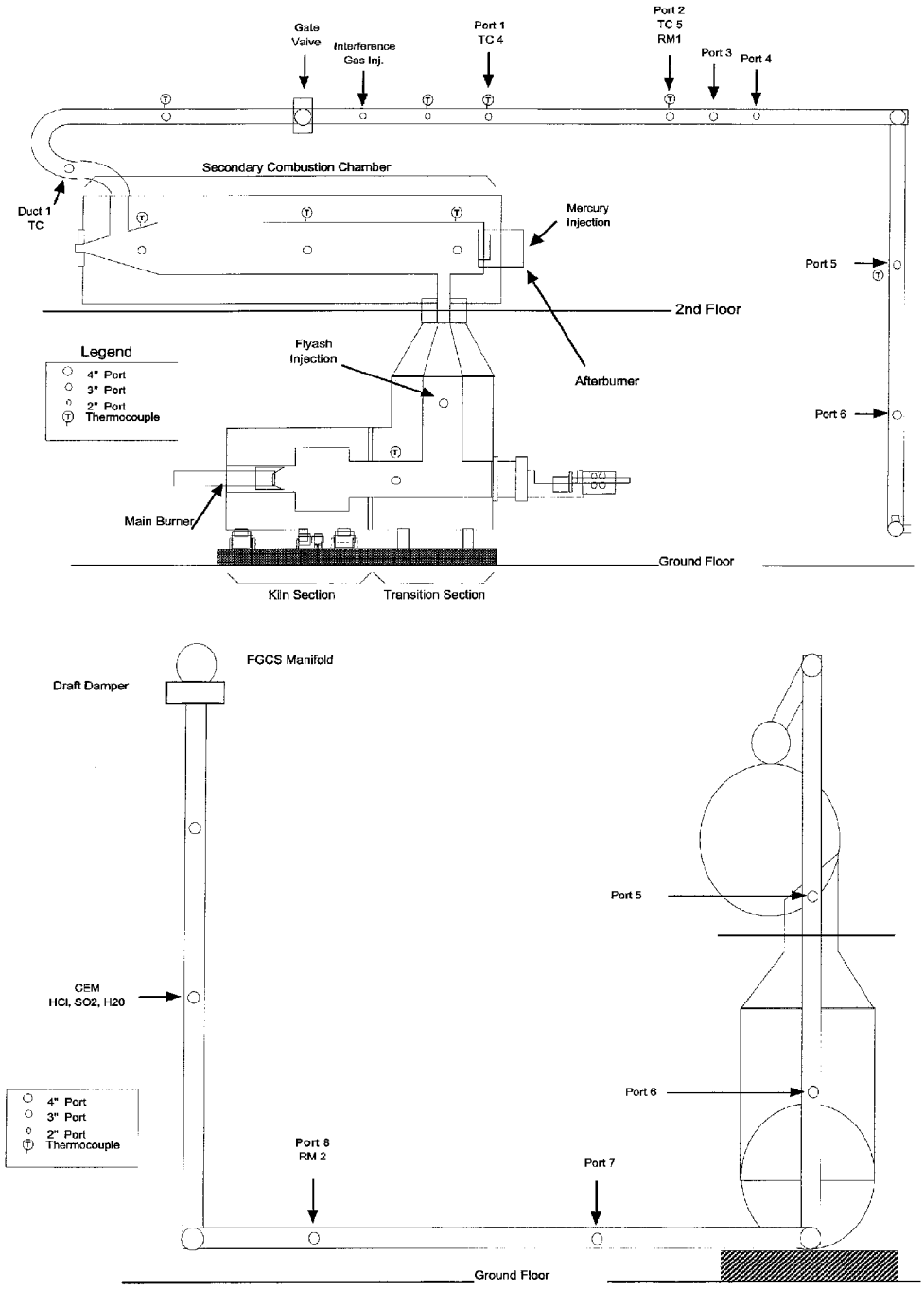

Figure 2. Side View (top) and End View (bottom) of the RKIS Test Facility

port opposite a 7.6-cm (3-in.) diameter port and a single 7.6-cm (3-in.) diameter port at right angles to the other two. Eight sets of ports are in place. The first set of ports is 4.3 m (14 ft) downstream from the air dilution damper. The second set of ports is 1.4 m (4.5 ft) downstream of the first set. Two additional sets of ports are located at 0.6-m (2-ft) intervals downstream, and the remaining ports are at about 2-m (6.6 ft) intervals further downstream. The Hg CEMs undergoing testing will be located at ports 5, 6, and 7 (Figure 2); the reference method sampling will take place at the locations labeled RM1 and RM2 (Figure 2).

Flue gas concentrations of oxygen (O_2), carbon dioxide (CO_2), carbon monoxide (CO), nitric oxide and total nitrogen oxides (NO/NO_x), SO_2, and hydrogen chloride (HCl) are monitored at the RKIS by means of CEMs for these species. These CEMs are calibrated and operated by EPA and/or contractor staff as part of the normal operations of the RKIS facility. These CEMs, which are identified in Table 2, can draw sample from various points in the duct. In this test, O_2 content will be measured just downstream of the air dilution damper and also in a section of duct downstream of the Hg CEM and reference method locations. Comparing the upstream to downstream O_2 measurement will verify that neither the tested CEMs nor the reference method sampling are causing air in-leakage resulting in flue gas sample dilution. Flue gas at the mercury CEM sampling locations will have a temperature of up to 340°C (650°F), an oxygen content of about 15%, and a moisture content of about 7% by volume. The duct is at a negative pressure (draft) of nominally 0.25 kPa (-1 in. water column). The volumetric flow rate is about 8.8 scm/min (310 scfm), resulting in flow velocities that are nominally 1.8 to 2.9 m/s (5.9 to 9.5 ft/s). Flow velocities are essentially constant across the duct diameter.

The RKIS facility CEMs have two major roles in a verification test. First, measurements of major diluent gases in the flue gas (O_2, CO_2) are used, along with H_2O content results obtained from the OH method, to assess air in-leakage as noted above and to establish the flue gas composition for adjustment of all test results to common conditions. Second, measurements of pollutants (CO, SO_2, NO/NO_x, HCl) are used to document normal flue gas composition and to establish the target levels of interferants added to the RKIS flue gas. That is, interferant levels are achieved by actual measurements in the duct using the RKIS CEMs, rather than by calculated dilutions of standards for SO_2, CO, etc., injected into the flue gas. In the case of NO_x, the injected interferant is NO; typically 5 to 10% of the injected NO is converted to NO_2 in the RKIS. HCl levels may be prepared by injecting HCl or chlorine gas (Cl_2) and monitoring with the RKIS

CEM for HCl. Injecting Cl_2 into the RKIS may produce both Cl_2 and HCl, depending on the point of introduction of the Cl_2. In such cases, the amount of Cl_2 in the flue gas is calculated as the amount injected minus the HCl measured by the HCl CEM. This approach is made necessary by the absence of a CEM for Cl_2.

Table 2. Summary of RKIS Pollutant CEMs

Pollutant	Instrument	Principle	Measurement Range(s)
O_2	Rosemount Analytical Model 755R	Paramagnetic	0-25%
CO_2	Horiba Model VIA510	NDIR[a]	0-20%
CO	Horiba Model PIR2000	NDIR	0-500 ppm
NO_x	TECO Model 10	Chemiluminescent	0-250 ppm
SO_2	Bodenzeewerk Model MCS 100	GFCIR[b]	0-250, 0-2500 ppm
HCl	Bodenzeewerk Model MCS 100	GFCIR	0-100, 0-1000 ppm

[a] NDIR = nondispersive infrared.
[b] GFCIR = gas filter correlation infrared.

3.2 RKIS Operation

For all tests, both the kiln and the afterburner are fired with natural gas. No waste or simulated waste feed to the kiln is employed; however, mercury is introduced into the flue gas by atomizing an aqueous solution of mercuric nitrate ($Hg(NO_3)_2$) into the afterburner. The mercury solution is atomized into an annulus inside the afterburner natural gas feed tube. The solution is atomized at the exit from that annulus, introducing Hg-containing aerosol droplets directly into the burner flame. The droplets evaporate rapidly in the flame zone, yielding primarily dry, vapor-phase Hg. The oxidation state of the Hg is manipulated by also introducing gaseous chlorine into the RKIS.

Two Hg solutions are used in the test to produce relatively low Hg levels, simulating those in coal-fired power plant flue gas, and much higher levels, simulating those in incinerator flue gas. In both cases, the solution addition rate will be nominally 10 liters per minute. The high concentration solution is diluted approximately ten-fold to make the solution for the lower

target concentration tests. The target low and high Hg concentrations are about 8 $\mu g/m^3$ and 80 $\mu g/m^3$, respectively.

Particulate matter is introduced into the flame zone to produce a particulate matter loading in the flue gas downstream. Particulate injection is needed primarily to create a realistic flue gas environment and also to provide a particulate Hg sample to verify the TM and PM measurement capabilities of CEMs that determine the PM component. A K-Tron mass-controlled feeder is used to inject coal flyash from a utility boiler directly into the hot flue gas as it exits the kiln. The flyash to be used was selected for its low reactivity with vapor-phase Hg and shall be thoroughly characterized for Hg content. The particulate loading during verification testing is determined using the filter and front half catch from the OH reference method trains, rather than from a separate Method 5 train. One OH train from each of the two reference sampling locations is used to determine particulate loading in each run.

In addition to Hg and particulate matter, other common flue gas constituents are introduced to simulate flue gas composition and evaluate potential interferences in Hg CEM measurements. Specifically, Cl_2, HCl, CO, SO_2, and NO are introduced by diluting compressed gases into the flue gas.

Hg solutions, particulate matter, or gases are injected only after stable operation of the RKIS is achieved, and the RKIS flue gas cleaning system is operating within its permit limits. Injection begins at least 30 minutes before any reference sampling or verification data collection takes place.

4 EXPERIMENTAL DESIGN

4.1 General Design

The verification test derived from this generic test protocol shall be conducted over about a three-week period at the test facility. The first week is spent installing the commercial CEMs and conducting a shakedown run of all systems before the verification effort begins. Testing does not begin until all the reference method equipment and test facilities are fully operational. Similarly, it is desirable that all the commercial CEMs be fully operational to participate in the verification test. However, to avoid delaying the start of the testing, all participating CEMs shall

be required to arrive at the facility by a specified day and be ready to begin testing within one week after arrival, or when the test facility itself is fully ready, whichever is later. CEMs that are not operational at that time may join the testing process once they come on line.

The two weeks of testing follow immediately after the setup/shakedown period. A similar test schedule is followed in each of the two weeks, but the Hg levels and the levels of other flue gas constituents are different in the two weeks. Verification involves comparing the CEM results with those from a time-integrated reference method (the OH Method),[4] as well as challenges with interferences and with Hg^o compressed gas standards. In general, different test activities are conducted on different days, but certain test procedures take place on every test day. All participating CEMs, and the reference method sampling trains, sample flue gas at the same time from the RKIS duct. However, it is not possible to collocate the sampling points of all the CEMs. Tests at the RKIS facility have shown that Hg concentrations are conserved in passage through the duct, so the exact location of individual CEMs is not expected to introduce bias in the verification.[5] Reference method samples are collected at both the upstream and downstream end of the duct in all verification testing to document the Hg levels and Hg speciation.

The performance parameters to be verified and the procedures with which they will be tested are summarized below:

- Relative accuracy—by comparison to reference method results on flue gas samples
- Correlation—with reference method results
- Precision—by repeated readings under stable conditions
- Calibration drift/zero drift—by sampling of Hg^o standard gas or zero gas
- Sampling system bias—by sampling of Hg^o standard gas both through the CEM's sampling probe and at the CEM's Hg analyzer
- Interferences—by addition of potential interferants to the flue gas
- Response time—by observation of instrument response with standard/zero gases
- Setup/maintenance Needs—by observation of installation and maintenance efforts
- Data completeness—by the fraction of the verification test completed.

Throughout the verification test, each CEM undergoing testing is operated by the CEM vendor's own staff. However, the intent of the testing is for the CEM to operate continuously in

a manner simulating operation at a combustion facility. **As a result, once the verification test has begun in each week of testing, no adjustment or recalibration is performed, other than what would be conducted automatically by the CEM in normal unattended operation. Adjustments to the CEM may be made between the first and second weeks of testing.** Repair or maintenance procedures may be carried out at any time, but testing is not interrupted; and data completeness will be reduced if such activities prevent completion of verification tests.

The schedule and procedures of this verification test are described in more detail in the subsequent sections.

4.2 Weekly Schedule

The Hg CEM testing follows the weekly schedule shown in Table 3. The first four days of the week are scheduled for verification test activities of various kinds, and the fifth day is scheduled to allow for any repeat tests or completion of items not completed on earlier days. A day for maintenance and a scheduled down day complete the week. As Table 3 shows, on Monday, Tuesday, and Wednesday of the test week, verification testing will consist of challenging each CEM with zero gas and a Hg^o gas standard in the morning, followed by flue gas sampling with both the CEMs and the reference method in the afternoon. As noted above, once the verification test has begun on Monday, no further adjustment of the CEM will take place until the end of the first week of testing. On Thursday and Friday of the first test week, the same Hg^o challenge is carried out in the morning, resulting in a series of five successive days for this test. On Friday morning, a sampling system bias test is also conducted, in which the Hg^o standard gas is first sampled through each CEM's sample interface, and then directly at the CEM's pollutant analyzer. Also on Friday morning, the response time of the CEMs is tested, using the Hg° standard gas. The afternoon of Thursday is devoted to testing interferences in the flue gas matrix, and part of the afternoon of Friday is used to perform a qualitative test of the CEM's ability to monitor Hg at levels below 5 $\mu g/m^3$. The rest of Friday afternoon is available to repeat tests from earlier days and to address any unforseen problems or opportunities in sampling.

Table 3. Weekly Schedule of Mercury CEM Verification Testing

Day	AM/PM	Test Activity (Performance Parameter)
Monday	AM	Challenge with Hg^o standard/zero gas (Calibration/Zero Drift)
	PM	Flue gas sampling (Relative Accuracy, Correlation, Precision)
Tuesday	AM	Challenge with Hg^o standard/zero gas (Calibration/Zero Drift)
	PM	Flue gas sampling (Relative Accuracy, Correlation, Precision)
Wednesday	AM	Challenge with Hg° standard/zero gas (Calibration/Zero Drift)
	PM	Flue gas sampling (Relative Accuracy, Correlation, Precision)
Thursday	AM	Challenge with Hg^o standard/zero gas (Calibration/Zero Drift)
	PM	Spiking of flue gas (Interferences)[a]
Friday	AM	Challenge with Hg^o standard/zero gas (Calibration/Zero Drift, Response Time,[a] Sampling System Bias)
	PM	Low level Hg response;[a] completion or repetition of tests
Saturday	AM/PM	Test preparations / Maintenance
Seven		Down day—no testing

[a] Test performed only in the first week of verification testing.

Saturday of the first week is used to prepare for the next week of testing or to maintain the test facility or other systems.

The second week of verification testing is similar to the first, except that the interference, response time, and low level Hg tests are not performed. As a result, testing activities in the second week are completed by Thursday. This schedule allows ample time for completion or repetition of any test activities.

The interference testing is conducted by establishing a stable Hg addition to the RKIS combustion zone, and then monitoring that Hg level continuously with the CEMs while adding other flue gas constituents one at a time or together. The effect of the interferants is assessed by comparing the CEM response with only Hg added with the response when Hg and one or more interferants are added. The Hg level used in this test is the 8-$\mu g/m^3$ level to be used in the first week of verification testing. The interferant levels used are relatively high to assure a definite conclusion about the presence or absence of an interference.

4.3 Test Conditions

Table 4 shows the approximate levels of Hg and other constituents to be prepared in the flue gas stream for each of the two weeks of testing. Conditions for the first week are intended to approximate those in a coal-fired power plant and in the second week, those in a municipal waste incinerator. The order of these two test conditions was chosen so that the lower Hg concentration is used first to avoid contaminating the RKIS during testing. The approximate levels shown in Table 4 shall be maintained throughout all periods of Hg addition and reference method sampling. The flue gas levels of all constituents in Table 4 should be maintained within 10% of the target levels shown.

Table 4. Summary of Flue Gas Constituent Concentrations Planned for Use in Verification Testing

Test Week	Hg ($\mu g/m^3$)	SO_2 (ppm)	NO_x (ppm)[a]	HCl (ppm)[b]	Particulate (mg/m^3)
One	8	1000	250	25	30
Two	80	50	150	100	30

[a] Produced by injection of NO.
[b] Produced by injection of stoichiometrically equivalent levels of Cl_2.

In all cases when reference method data are being taken, the introduction of the indicated constituents shall be held constant throughout the entire sampling period. The intent of this approach is to allow comparisons of CEM data with reference method data under constant conditions. Higher levels of flue gas constituents are used in the interference testing, as described in the next section.

4.4 Test Procedures

The RKIS should be operated continuously during the entire test period and should not be shut down overnight. Such continuous operation is intended to minimize the potential for retention and subsequent release of Hg by the refractory or other components of the RKIS. The Hg CEMs undergoing verification are located at ports 5, 6, and 7 of the RKIS (see Figure 2). Locations indicated as RM1 and RM2 in Figure 2 are reserved for reference method sampling,

which is performed by contractor staff. The sampling ports are assigned so that no CEM is affected by the operation of any other CEM upstream.

At the beginning of each test day, the CEMs undergoing testing are supplied (one at a time) with zero gas and then with a commercial compressed gas standard containing elemental Hg. The response to each gas shall be recorded on each test day to assess the zero and calibration drift of the CEMs. In this test, the Hg standard is used solely as a stable, clean sample matrix, not as an absolute Hg standard. On one test day in the first week of testing, the rise and fall times of the CEMs are determined by recording their readings as the Hg^o gas is first turned on and later turned off. Also on one day in each week of testing, the Hg^o standard gas is delivered first directly to the CEM's Hg analyzer, and then through the CEM's sample interface, to assess bias introduced by the interface itself.

During the drift checks, the reference method sampling trains are assembled and leak checked, and the RKIS combustion gas CEMs are calibrated in accordance with facility standard operating procedures. At this time, the RKIS operation is stabilized at the desired incineration conditions firing natural gas. After stable RKIS operation is achieved (as indicated by readings of O_2, temperature, and gaseous emissions, e.g., CO, NO_x), injection of Hg spike solution to give the day's target flue gas concentration is initiated. Hg solution is fed to the RKIS for at least 30 minutes before reference method sample initiation. The addition of the other flue gas constituents will follow this same procedure. The Hg CEMs begin recording data as soon as they are brought on line. However, the reference method sampling starts no sooner than a time previously agreed upon with the CEM vendors. The CEM vendors are given at least 15 minutes notice prior to initiating reference method sampling.

The number of reference method samples collected depends on the target Hg concentration. The reference method sampling time shall be approximately three hours with the low Hg levels present in the first week of testing and approximately one hour with the higher Hg levels in the second week. This duration of sampling allows two reference method samples per day (6/week) in the first week of testing and three per day (9/week) in the second week. During verification testing, sampling is conducted simultaneously with four trains of the OH method, two each at the upstream and the downstream ends of the RKIS duct. Thus, each of the two or three measurement periods during a test day provides four OH results for comparison with the CEM data. To ensure that the reference method and CEM data sets are indeed parallel and comparable

for each period, the CEM vendors shall be notified of the start and stop times of each reference method period, so they can report average analyte concentrations that correspond directly to the reference method measurement period.

The OH sampling trains sample isokinetically from a single point in the center of the RKIS duct (i.e., no traversing because of the small size of the duct). The CEMs undergoing testing also sample at a single point in the center of the duct, non-isokinetically. Each CEM operates with a simple stainless steel probe and a heated filter and heated transfer line that mimic those used with the OH trains. The temperature of the heated filters shall be approximately 250°F, sufficient to keep the sample gas above its dew point; no attempt shall be made to maintain the sample gas at its stack temperature. An EPA Method 2 traverse shall be done at each reference sampling location before and after OH sampling. The pre-run traverse shall be used to set the isokinetic sampling rate. The average of the pre- and post-sampling traverses shall be used for final calculations.

The chemical analysis of recovered sample fractions from OH method trains shall be conducted by contractor staff, using contracted laboratory facilities currently used for mercury research studies at the RKIS. Sample handling, analysis, and all associated QA/QC activities will conform to the requirements of the OH method.[4] Samples shall be recovered from the OH trains within about two hours after sample collection and delivered to the analytical laboratory within 48 hours of sample collection. Samples are refrigerated until transfer to the analytical laboratory. Unique sample identification numbers are implemented so that final data used for verification can be traced back through the analytical process to the original sample. Field blank samples are recovered from one blank sampling train on each day that OH method samples are collected. Before sample recovery, that blank train is transported to the upstream or downstream sampling location at the RKIS on alternate days. Care shall be taken that the blank train is selected at random from the prepared trains, so that different trains are used as the blank on different days.

The daily schedule for the first three test days (Monday to Wednesday in Table 3) is illustrated in Figure 3. That figure shows the schedule for a day in the first week of testing when two three-hour OH runs are conducted. In the second week, three one-hour runs will be conducted each day.

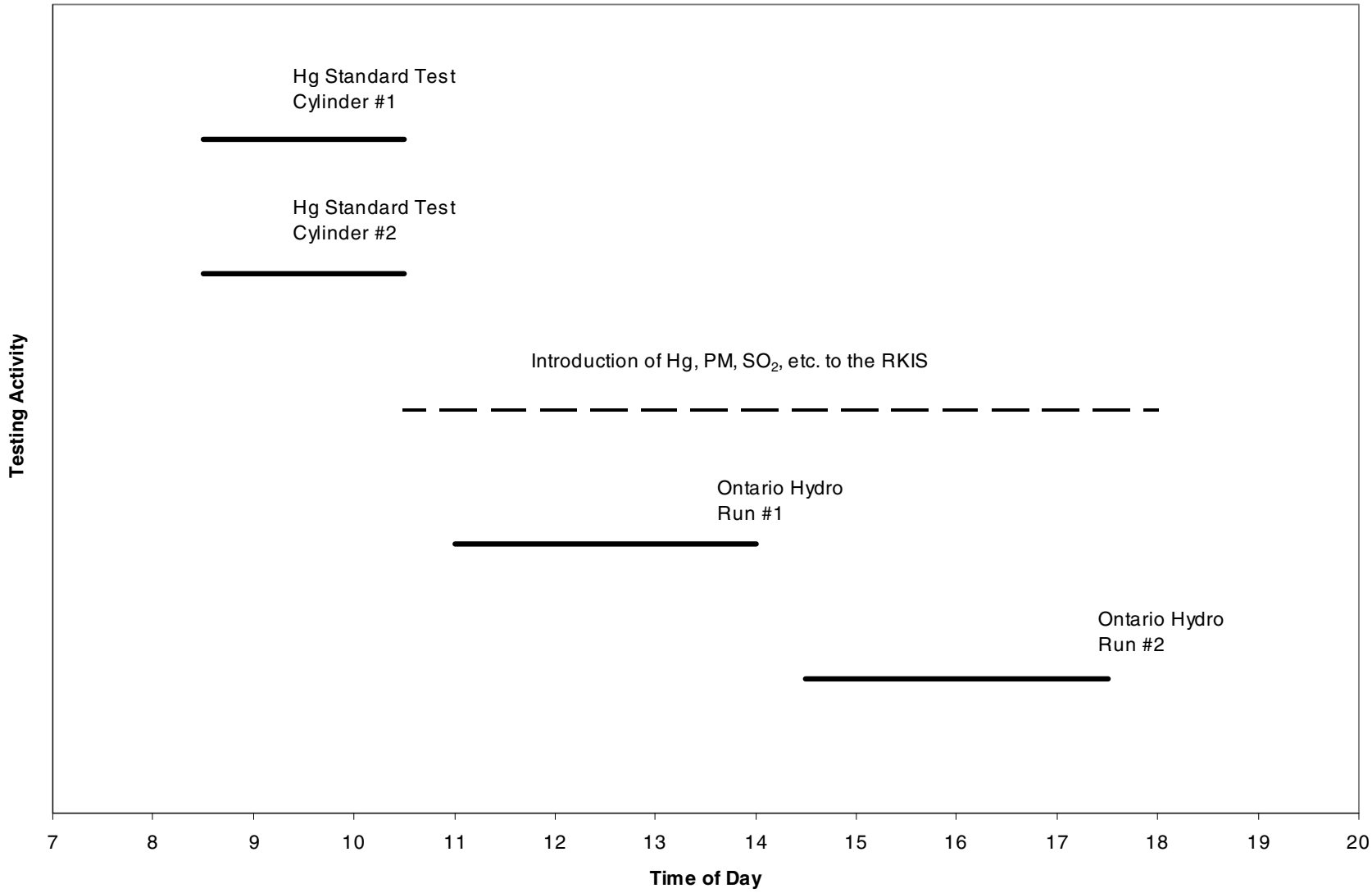

Figure 3. Schedule of Verification Test Day with Ontario Hydro Sampling

Following the completion of the Hg° standard gas test, Hg, SO_2, particulate matter, etc., shall be introduced to the RKIS. As shown in Figure 3, introduction of these species into the RKIS begins at least 30 minutes before the start of the first OH run and continues until the last OH run is completed. The flue gas composition is maintained in this period at the levels shown in Table 4.

The schedule of the day on which interference is tested (Thursday in Table 4) is shown in Figure 4. The same Hg° standard gas challenges are done in the morning as described above in the context of Figure 3. Then a stable Hg level is introduced into the RKIS, and the response of the CEMs being tested is allowed to stabilize. Then each of several potential interferants is also introduced into the RKIS duct, one at a time for periods of at least one-half hour. The interferant gases and the levels to be introduced in this test are listed in Table 5. After the last individual interferant (Cl_2) has been tested alone, the Cl_2 addition is continued, and the NO addition is resumed to assess whether the combination of NO_x and Cl_2 produces an interference. Subsequently, the other gases (SO_2, CO, HCl) also are injected to produce a mixture of all five interferants at the concentrations shown in Table 5. Finally, all the interferants are shut off, and measurements are made again with only the Hg injection taking place. Throughout the test, the Hg injection is held constant, and the Hg CEM responses in the presence of interferants are compared to those with only Hg injected into the RKIS.

Table 5. Interferant Gases and Concentrations to Be Used in Interference Testing

Interferant	Concentration
NO_x (NO addition)	500 ppm
SO_2	2000 ppm
CO	500 ppm
HCl	250 ppm
Cl_2	10 ppm

A final test assesses qualitatively the ability of the Hg CEMs to measure Hg levels below 5 $\mu g/m^3$. This test shall be conducted on Friday of the first test week (Table 3), by starting with no Hg injection, then establishing a 0.5 $\mu g/m^3$ Hg level, and then increasing the Hg concentration in successive steps of two, i.e., to 1 $\mu g/m^3$, then to 2 $\mu g/m^3$, then to 4 $\mu g/m^3$. No absolute comparison of CEM results to OH method results methods is made in this test. However, the

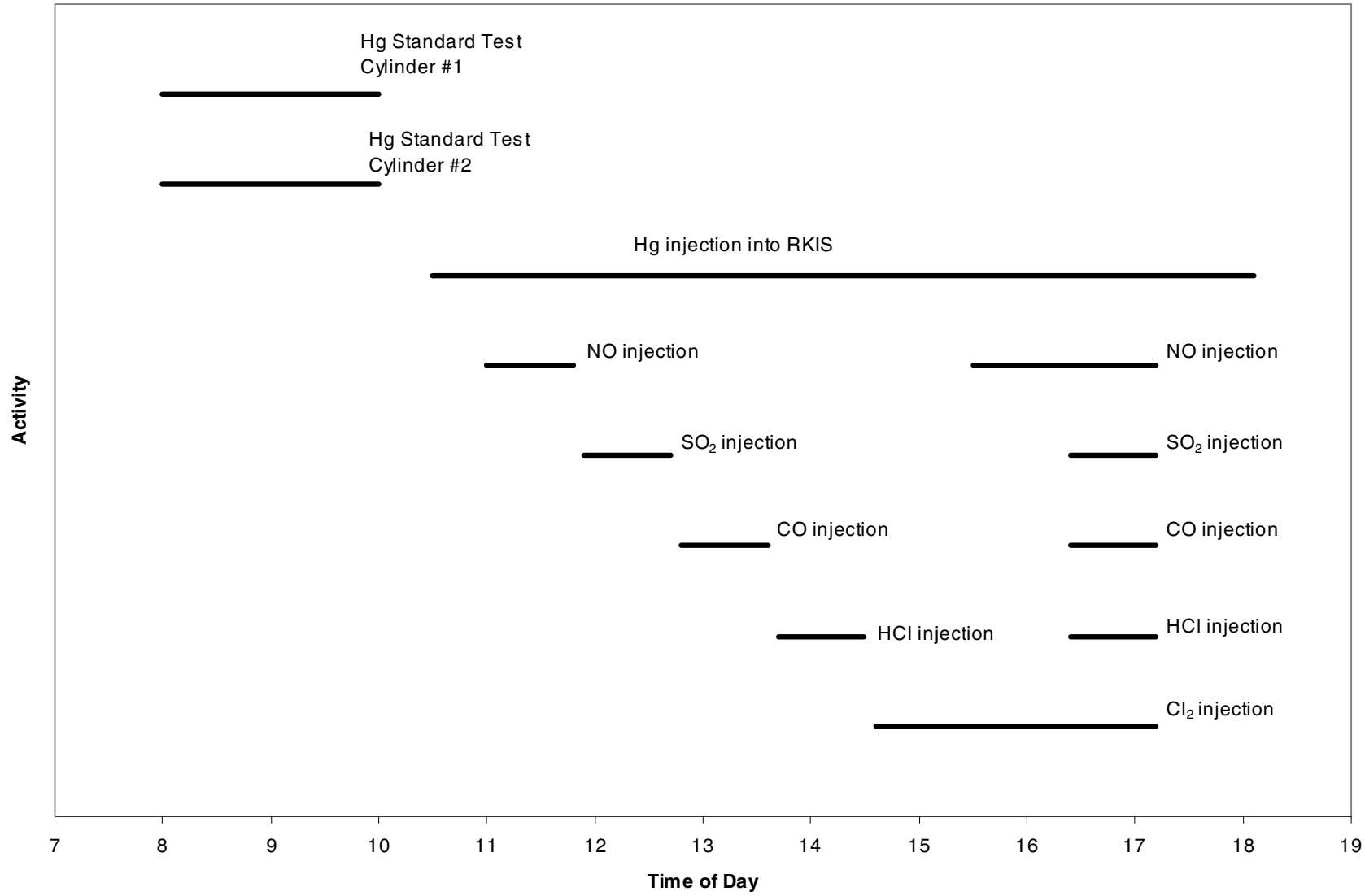

Figure 4. Schedule of Interference Test Day

introduction of Hg to the RKIS can be easily and accurately changed and provides a valuable test of Hg detection. This test is conducted after an overnight period in which no Hg has been introduced into the RKIS, assuring that background Hg levels are as low as possible prior to injecting Hg. Figure 5 shows the daily schedule of activities for this test procedure. The response of each CEM with varying levels of Hg addition is compared to that with no Hg addition, and the lowest Hg level producing a positive response is reported. The remainder of the test day after completion of the low-level Hg test is used to repeat or finish other test activities as necessary, as indicated in Table 3.

4.5 Data Comparisons

This section describes the use of reference and CEM data. Data used for the verification comparisons are summarized in Table 6.

Relative accuracy shall be verified by comparing the CEM results against the reference results for each parameter that the CEM measures. That is, if the CEM measures only total vapor-phase Hg, then only the TVM results from the OH method are used for verification. However, if the CEM also measures oxidized, elemental, or particulate Hg, then those results from the OH method also are used for verification. A total of 15 OH sampling runs shall be used in the verification test (six with lower Hg levels, and nine with higher Hg levels), with four OH sampling trains operating simultaneously in each period. Thus, a total of 60 OH samples shall be used to evaluate relative accuracy.

The purpose of sampling with dual OH trains at both reference sampling locations is to assess the variability of the reference method results that are the basis for the CEM verification. At the Hg concentrations to be used in a verification task, it is expected from previous results that the precision of duplicate OH results will be within about 10%. On the basis of those same results, it is expected that day-to-day reproducibility of Hg levels in the RKIS, and upstream-to-downstream uniformity of the Hg levels, also will be within that range. Thus, consistent Hg levels are expected throughout each week of testing. As a result, the entire set of reference method results, not merely those from a single test day, shall be considered in screening for reference data quality. The OH results shall be reviewed before verification comparisons are

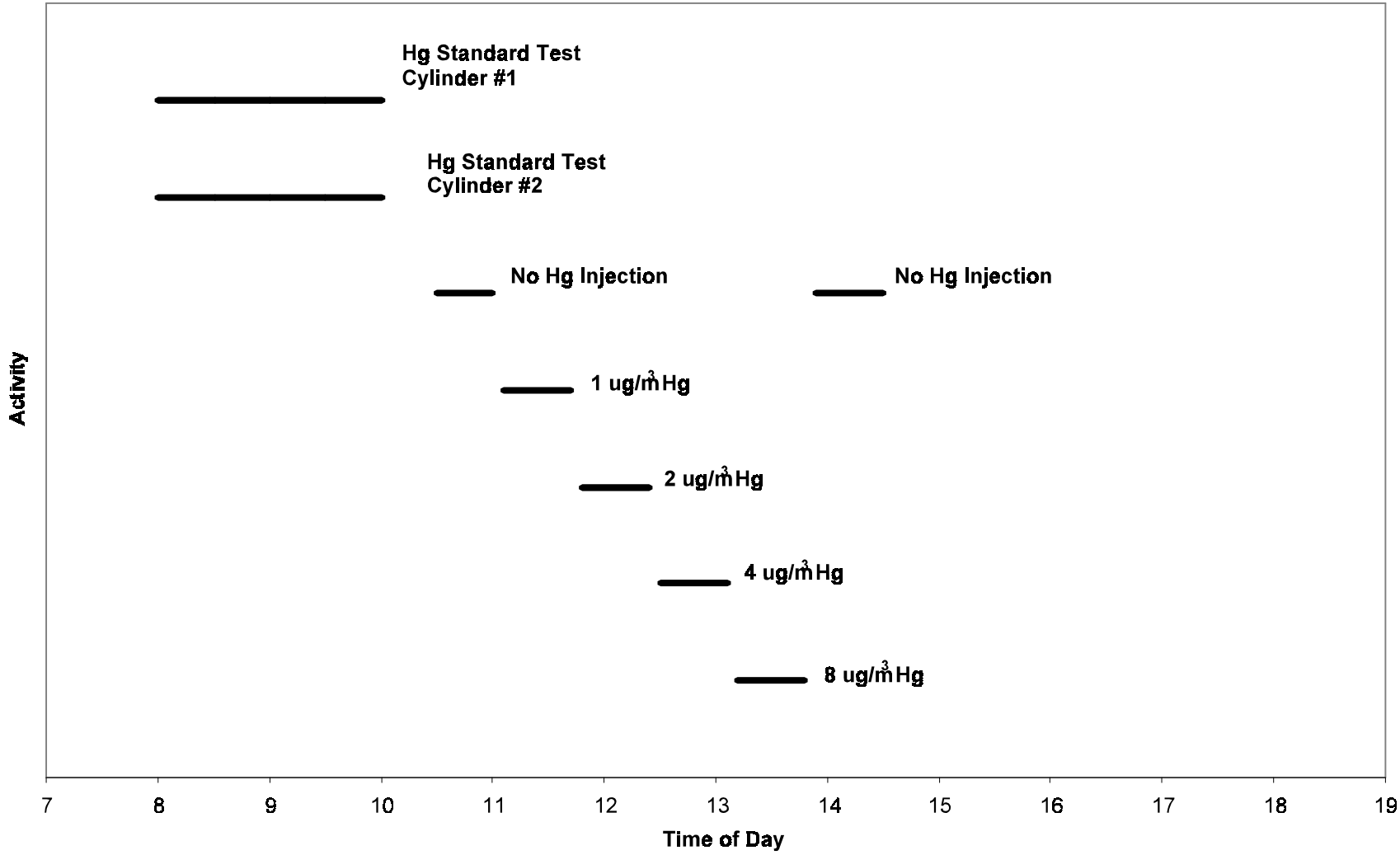

Figure 5. Schedule for Low-Level Hg Detection Test

Table 6. Summary of Data to be Obtained in Mercury CEM Verification Test

Performance Parameter	Objective	Comparison Based On	Total Number of Data Points for Verification
Accuracy	Determine degree of quantitative agreement with reference method	Reference method results	60[a]
Correlation	Determine degree of correlation with reference method	Reference method results	60[a]
Precision	Determine repeatability of successive measurements at fixed mercury levels	Repetitive measurements under constant facility conditions	15[b]
Cal/Zero Drift	Determine stability of zero gas and span gas response over successive days	Zero gas and Hg^o standard	9[c]
Sampling System Bias	Determine effect of the CEM's sample interface on response to zero gas and Hg^o standard	Response at analyzer *vs.* through sample interface	2[d]
Interferences	Determine the effect of interferants on response to a constant Hg concentration	Observation of CEM response with and without added interferants	7[e]
Response Time	Estimate rise and fall times of the CEMs	CEM results at start/stop of Hg addition	4[f]
Low-Level Hg Response	Determine ability of CEMs to respond to Hg below 8 $\mu g/m^3$	Continuous monitoring of varied Hg concentrations	5[g]

[a] Number of data points refers to total number of OH method sampling runs used for comparison. Each run will provide a value for TM, OM, EM, and PM.

[b] Based on the total number of OH method sampling runs in which repeatability of CEM results will be assessed.

[c] Based on total number of zero/span challenges done in the two weeks of testing.

[d] Based on conducting this test once in each week of testing.

[e] Based on tests for SO_2, CL_2, NO_x, CO, HCl, and mixtures of these species done in the first week of testing.

[f] Based on rise and fall time tests with pure gases, in each of the two weeks of testing.

[g] Based on response to 0, 0.5, 1, 2, and 4 $\mu g/m^3$ Hg levels.

made to identify individual outliers from the full set of reference method results. That is, the OH results shall be screened for three factors:

- Precision of results from collocated sampling trains
- Consistency of results with others at the respective sampling locations
- Uniformity of upstream and downstream locations.

OH test results that are identified as outliers on any of these criteria are reported, but will not be used for verification. The intent of this approach is to provide a valid set of reference data for verification purposes, while also illustrating the degree of variability of the reference method. Identification of outliers is based on basic statistical tests such as a *t*-test comparison of means or a Q-test evaluation of divergent results. In any case, where rejection of a reference result is suggested, an effort shall be made to find an assignable cause for the divergent result.

Correlation of the CEM with the OH method shall be verified using the same data used to assess relative accuracy. Correlation is calculated for each parameter measured by the CEM (i.e., TVM, EM, OM, etc.).

Precision of the CEMs shall be assessed based on the individual measurements performed by each CEM over the duration of each OH method sampling run. For example, if a CEM provides an updated measurement every five minutes; then over a one-hour sampling run, a total of 12 readings would be obtained. The average and standard deviation of those readings is calculated to assess precision. This procedure is applied to all 15 of the OH method sampling intervals.

Calibration and zero drift shall be verified based on challenging the CEMs with zero gas and with a compressed gas standard of Hg^o on each test day in each week of the test. Thus, at least nine data points are used to assess zero drift and an equal number to assess calibration drift. Note that only the relative stability of the response is assessed, i.e., the Hg^o standard is not used as an absolute calibration standard. The sampling system bias test is performed once, as part of the calibration/zero drift test procedure, in each week of testing.

Interference effects shall be assessed by adding potential interferants one at a time during a constant addition of Hg to the RKIS flue gas and comparing the CEM readings with and without the interferant. This is done only in the first week of testing (i.e., at the lower Hg level)

for the seven individual interferants or combination of interferants described in Section 4.4. Thus, a total of seven comparisons shall be made of interference effects.

Response times shall be determined by recording successive CEM readings at times when Hg delivery to the CEM is started or stopped. This procedure is performed once in each test week as part of the calibration/zero drift test, using the Hg^o standard gas. Both rise and fall time are determined, resulting in two determinations of rise time and two of fall time.

Low-level Hg response shall be evaluated once in the first test week by successively reducing the Hg level in the RKIS. The lowest Hg level giving a response above the zero air reading is reported.

No additional test activities shall be required to determine the data completeness achieved by the CEMs. Data completeness shall be assessed by comparing the data recovered from each CEM to the amount of data that would be recovered upon completion of all portions of these test procedures.

Setup and maintenance needs shall be documented qualitatively, both through observation and through communication with the vendors during the test. Factors to be noted include the frequency of scheduled maintenance activities, the downtime of the CEM, and the number of staff operating or maintaining it during the verification test.

5 STATISTICAL CALCULATIONS

The statistical calculations to be used to verify CEM performance are described below. In all cases, measurement results from both the reference method and the CEMs undergoing testing are to be reported in units of $\mu g/m^3$ on a dry basis at 20°C, 1 atmosphere pressure, and the actual flue gas O_2 content.

5.1 Relative Accuracy

The relative accuracy of the CEMs with respect to the reference (OH) method shall be assessed by:

$$RA = \frac{|\bar{d}| + t^{\alpha}_{n-1}\frac{S_d}{\sqrt{n}}}{\bar{x}} \times 100\% \quad (1)$$

where *d* refers to the difference between the OH and CEM results, and *x* corresponds to the OH result. S_d denotes the sample standard deviation of the differences, while t^{α}_{n-1} is the t value for the 100(1 - α)th percentile of the distribution with n-1 degrees of freedom. The relative accuracy is determined for an α value of 0.025 (i.e., 97.5% confidence level, one-tailed). The relative accuracy calculated in this way can be interpreted as an upper confidence bound for the relative bias of the analyzer, i.e., $\frac{|\bar{d}|}{\bar{x}}$, where the superscript bar indicates the average value of the differences or of the reference values. Relative accuracy is calculated separately for the first and second week of testing, with up to 24 samples and up to 36 samples, respectively (assuming all OH method samples can be treated as independent results). With these numbers of samples, the relative accuracy procedure stated in PS-12[6] shall be followed, i.e., up to three results may be omitted from the relative accuracy calculation. The impact of the number of data points (n) on the relative accuracy value shall be noted in the verification report. Relative accuracy shall be calculated separately for each parameter measured by each CEM (i.e, TVM, EM, OM, etc.).

5.2 Correlation with Reference Method

The degree of correlation of each CEM with the reference method results shall be assessed in terms of the coefficient of determination (r^2), which is the square of the correlation coefficient (r). The coefficient of determination is calculated for each parameter measured by each CEM (i.e, TVM, EM, OM, etc.). This calculation is made separately for the first and second week of testing, with up to 24 samples and up to 36 samples, respectively (assuming all OH method samples can be treated as independent results).

5.3 Precision

Precision shall be calculated in terms of the percent relative standard deviation of a series of CEM measurements made during stable operation of the RKIS, with Hg injected at a constant

level into the combustion zone. During each OH method sampling run, all readings from a CEM undergoing testing are recorded, and the mean and standard deviation of those readings are calculated. Precision (*P*) is then determined as

$$P = \frac{SD}{\overline{X}} \times 100 \qquad (2)$$

where *SD* is the standard deviation of the readings and $\overline{X}$ is the mean of the readings. The same calculation is performed for each parameter measured by the CEM (i.e., TM, EM, OM, etc.). This calculation is done for each CEM, using data from every OH method sampling run (15 in all). The verification report shall note that the calculated precision is subject to the variability of the test facility, not only the CEM variability. However, since precision is assessed for all CEMs based on data from the same reference sampling periods, the relative precision of the tested CEMs will be apparent. Although no comparison among CEMs is made, all CEM data from the periods of precision testing shall be reviewed to assess whether the consensus of the CEM data indicates a variation in the test facility itself. If such a variation is indicated, that finding shall be noted in all verification reports.

5.4 Calibration and Zero Drift

Calibration and zero drift is determined in a relative sense, rather than as deviations from an absolute standard, as in PS-12. That is, calibration and zero drift will be reported in terms of the mean, relative standard deviation, and range (maximum and minimum) of the readings obtained from the CEM in the daily sampling of the same Hg^o standard gas and of zero gas. Up to five Hg^o standard readings, and up to five zero readings, are used for this calculation in each of the two weeks of verification testing. The relative standard deviation is calculated as

$$RSD = \frac{SD}{\overline{x}} \times 100 \qquad (3)$$

where $\bar{x}$ is the mean, and *SD* the standard deviation of the daily readings on standard or zero gas. This calculation, along with the range of the data, indicates the day-to-day variation in zero and standard readings.

5.5 Sampling System Bias

Sampling system bias shall be calculated as the difference in CEM response when sampling Hg^o standard gas through the CEM's entire sample interface, compared to that when sampling the same gas directly at the CEM's pollutant analyzer, expressed as a percentage of the response at the analyzer. That is,

$$B = \frac{R_{si} - R_a}{R_a} \times 100 \quad (4)$$

where *B* is the percent bias, R_{si} is the CEM's reading when the standard gas is supplied at the sampling inlet, and R_a is the reading when the standard is supplied to the analyzer.

5.6 Interferences

Interferences shall be determined during sampling of combustion flue gas, in terms of the difference in response to a constant Hg level when a single interferant is added or removed. Interferences are quantified in terms of the relative sensitivity to the interferant species. The relative sensitivity is calculated as the ratio of the observed change in response of the analyzer to the concentration of the interferant. For example, a CEM that reports 8 $\mu g/m^3$ of total Hg in the absence of SO_2, may report 12 $\mu g/m^3$ in the presence of 500 ppm SO_2. The relative sensitivity of the CEM is thus 4 $\mu g/m^3$/500 ppm.

5.7 Response Time

The response time shall be determined as the time after a step change in Hg concentration when the CEM reading has reached a level equal to 95% of that step change. Both rise time and

fall time shall be determined. CEM response times are determined in conjunction with a calibration/zero drift check, by starting or stopping delivery of the Hg^o standard gas to the CEM's sampling interface, recording all readings until stable readings are obtained, and then estimating the 95% response time. For most CEMs, the estimation process requires interpolating between successive readings, since the measurement process is not truly continuous.

5.8 Low-Level Hg Response

The ability of the commercial CEMs to determine low Hg concentrations shall be assessed by comparing responses at successive levels of 0, 0.5, 1, 2, 4, and 0 $\mu g/m^3$ of added Hg in the RKIS. The lowest Hg level producing a response above that with no Hg added shall be reported. The data from all CEMs are reviewed collectively to indicate whether absence of a response may be a result of limitations of the Hg injection process or of limitations of CEM response. For example, if no CEM shows a response at the 0.5 $\mu g/m^3$ level, then no conclusion is drawn about detection of that level, since inadequate injection, rather than lack of detection, may be the cause.

6 MATERIALS AND EQUIPMENT

6.1 Gases and Chemicals

6.1.1 Interference Gases

Compressed gases (SO_2, NO, CO, HCl, Cl_2) for use in simulating combustion gas composition and testing interference effects shall be obtained from a commercial supplier and should be of a minimum 99% purity. Each interference gas consists of a single interferant as a pure gas.

6.1.2 High-Purity Nitrogen/Air

The high-purity gases used for zeroing of the CEMs shall be commercial ultra-high purity (i.e., minimum 99.999% purity) air or nitrogen.

6.1.3 Mercury Standard Gases

Two compressed gas standards containing elemental Hg shall be obtained from Spectra Gases for use in assessing the drift of the CEMs. These shall consist of Hg^o in a nitrogen matrix, at levels of about 1 ppb (8 $\mu g/m^3$) and 5 ppb (40 $\mu g/m^3$), for use in the first and second weeks of testing, respectively. Multiple cylinders of uniform concentration shall be obtained, if required to meet the gas consumption rates of the CEMs during the test. Each Hg°standard cylinder shall be analyzed both before and after the verification test by sampling the cylinder contents with EPA Method 101A and analyzing for Hg.

6.1.4 Injection Mercury Solutions

The solutions used to introduce Hg into the primary combustion zone of the RKIS shall be made from commercial American Chemical Society (ACS) reagent grade mercury (II) nitrate monohydrate (minimum 98% purity), or mercuric chloride ($HgCl_2$) using deionized water. A measured mass of the reagent is dissolved in deionized water with 25 milliliters of concentrated nitric acid (70 wt. percent, ACS reagent grade), and diluted to 4 liters with deionized water. Serial dilutions of this stock solution produce the working injection solutions. Each such solution is made by diluting an aliquot of the stock solution, along with 25 milliliters of the nitric acid, in deionized water, up to a 4-liter volume. All solution concentrations are calculated and reported in terms of Hg. The concentration of the injection solution must be known to calculate Hg feed rate and to fulfill RKIS permit reporting requirements. In terms of verification testing, while Hg injection solution concentrations and feed rates aid in establishing the appropriate flue gas Hg concentrations, the actual flue gas Hg content shall be determined by the OH method sampling and not by calculating the injected Hg. Solutions shall be made up only as needed for injection into the

RKIS, to minimize waste. All stock and injection solutions shall be prepared under the direction of the facility manager.

6.1.5 Mercury Spiking Standard

A National Institute of Standards and Technology (NIST)-traceable aqueous Hg standard, obtained from a commercial supplier, shall be used as the spiking solution in the performance evaluation (PE) of OH analysis noted in Section 7.2.2. If spiking the particle filter in the OH train is required in the PE of CEM determinations of particulate Hg, then a NIST coal flyash standard reference material shall be used as the spiking material.

6.2 Reference Method

6.2.1 Sampling Trains

The glassware, filters, and associated equipment for the OH reference method[4] sampling shall be supplied by EPA at the RKIS facility. Multiple trains shall be supplied so that as many as 12 trains (i.e., three sampling runs with four trains each) may be sampled in a single day, in addition to at least one blank train per day. Preparation, sampling, sample recovery, and cleaning of used trains is the responsibility of the test facility.

6.2.2 Analysis Equipment

Laboratory equipment for sample recovery and analysis shall be provided by the test facility. This includes all chemicals and solutions for rinsing train components and recovering impinger samples, as well as CVAA or CVAFS equipment for Hg determination.

6.3 RKIS Monitoring Equipment

Verification tests use monitoring equipment already integrated into the test facility. At the RKIS facility, this equipment includes monitors for major flue gas constituents (O_2, CO_2) and for

chemical contaminants (CO, NO_x, SO_2, HCl), as well as sensors for temperature and pressure. These monitors are identified in Table 2. These devices are considered part of the RKIS facility for the purpose of a verification test and are operated according to normal RKIS procedures.

6.4 Equipment Used for Performance Evaluation Audits

As described in Section 7.2.2, PE audits shall be performed for the O_2, CO_2, temperature, and pressure measurements in the RKIS flue gas. Those PE audits are performed by conducting a parallel measurement using an independent monitoring device. The devices to be used are provided by Battelle and may include the following:

- Paramagnetic O_2 monitor
- Infrared CO_2 monitor
- Thermocouple temperature indicator
- Aneroid barometer
- Magnehelic differential pressure indicator.

These devices shall have been calibrated by the manufacturer or by Battelle's Instrument Laboratory within the six months immediately preceding the verification test. In addition, a calibrated set of weights shall be used to audit the balance used to weigh impingers from the OH trains for determining flue gas H_2O content.

7 QUALITY ASSURANCE/QUALITY CONTROL

7.1 Equipment Calibration

7.1.1 Test Facility Monitoring Equipment

The test facility CEMs and other monitoring devices noted in Section 6.3 shall be calibrated by EPA and contractor staff according to normal facility procedures. However, a

distinction must be made between those measurements that factor directly into verification results, and those which are secondary in nature.

Measurements that factor directly into verification results are those that are used in calculating results from the OH method. Those include flue gas temperature, pressure, and O_2 and CO_2 content. For these measurements, compliance-level calibration procedures are required and shall be carried out by appropriate test facility staff. The pertinent calibration procedures shall be conducted on a schedule chosen by this staff, and suitable to assure adequate data quality during the verification. All calibration results must be documented for inclusion in the verification data files and verification report. The flue gas H_2O content is determined from impinger weights in the OH trains. Calibration records for the balance used shall be documented.

Measurements that do not factor directly into verification results include monitoring the pollutant gases CO, NO_x, SO_2, and HCl. These data indicate the level of flue gas constituents during interference testing or flue gas sampling. Calibration of the CEMs for these species need not meet compliance requirements, although, for some species, such calibration requirements may be in place due to the emission limits on the RKIS itself. For these species, single-point calibrations during the verification test, coupled with existing documentation of linear response, are sufficient.

7.1.2 Reference Method

The facility performing the OH method sampling must perform all required QA/QC activities stated in the method. This includes providing blank sampling trains (one per sampling day at either the upstream or downstream location) and blank sampling materials (filters, reagent solution blanks) in the field. Documentation of these activities is required for inclusion in the verification data file. Deviation from the OH method shall occur only in that the duct will not be traversed. Options for making particulate mass measurements, and for quickly turning glassware around in sample recovery, shall be used. OH trains shall be spiked by Battelle staff as recommended in the OH method (Section 7.2.3 of the method).

7.1.3 Analytical Laboratory

The laboratory analyzing the samples from the OH method must document all required calibrations conducted on the mercury analysis equipment. That documentation may be provided as part of an overall data package that includes the analytical results.

7.2 Audits

7.2.1 Technical Systems Audits

The Battelle Quality Manager shall perform a TSA once during a verification test. The purpose of this audit is to ensure that the verification test is being performed in accordance with the AMS Center QMP[1] and this test protocol and that all QA/QC procedures are being implemented. In this audit, the Battelle Quality Manager may review the reference sampling and analysis methods used, compare actual test procedures to those specified in this protocol, and review data acquisition and handling procedures. The Battelle Quality Manager shall prepare a TSA report, the findings of which must be addressed either by modifications of test procedures or by documentation in the test records and report.

At EPA's discretion, EPA QA staff also may conduct an independent on-site TSA during the verification test. The TSA findings shall be communicated to testing staff at the time of the audit and documented in a TSA report.

7.2.2 Performance Evaluation Audit

A PE audit shall be conducted to assess the quality of the measurements made in this verification test. This audit should address only those measurements that factor into the data used for verification, i.e., the CEMs being verified and the vendors operating these CEMs are not the subject of the PE audit. This audit is performed once during the verification test and must be performed by comparing Battelle measurements with a standard or a reference that is independent of standards used during the testing. For most of the key measurements, this audit shall be done by comparing data from the RKIS equipment to that from a second analyzer or monitor operated

simultaneously. For example, the PE audit of O_2 data involves sampling with a second O_2 analyzer at the same point in the duct and comparing results. Similar comparisons shall be made for temperature, pressure, and CO_2. In addition, the balance used to determine flue gas H_2O content by means of the OH impinger samples shall be checked with a calibrated set of weights. Table 7 summarizes the PE audits that will be done. These audits are the responsibility of Battelle staff and shall be carried out with the cooperation of EPA and test facility staff.

Table 7. Summary of PE Audits on Test Facility Measurements

Parameter	Audit Procedure	Expected Tolerance
O_2	Compare to independent O_2 measurement	±1% O_2
CO_2	Compare to independent CO_2 measurement	±10% of CO_2 reading
Temperature	Compare to independent temperature measurement	±2% absolute temperature
Barometric Pressure	Compare to independent pressure measurement	±0.5 inch of H_2O
Flue Gas Differential Pressure	Compare to independent pressure measurement	±0.5 inch of H_2O
Mass (H_2O)	Check balance with calibrated weights	±1% or 0.5 g, whichever is larger

These PE audits shall be carried once during the period of operation at the test facility. Battelle supplies the equipment needed to make the independent PE measurements. If agreement outside the indicated tolerance is found, the test is repeated. Further failure to achieve agreement results in recalibrating the independent measurement device or using a different measurement device.

For Hg, this PE requirement is difficult because of the absence of convenient absolute gas-phase Hg standards or independent measurement devices. Consequently, this audit consists of spiking one or more OH sampling trains with known amounts of Hg and conducting sample analysis on the train without sampling combustion gas. If the CEMs undergoing verification do not determine particulate Hg, then only the impingers of the OH train are spiked. A NIST-traceable Hg standard solution is used for that purpose. Agreement of Hg determined in sample analysis with that spiked into the sample train is expected to be within 10%. Because of the time

required for sample analysis, the PE audit results for Hg may not be known until after the verification tests are completed. The response to PE audit results outside the expected tolerance is to consider possible causes for the disagreement and, if appropriate, to note in the verification reports the implications of OH PE results on CEM verification results. If one or more of the CEMs undergoing verification determines particulate Hg, then a Hg standard also is used to spike the particle filter in the OH train. Battelle's Quality Manager shall assess PE audit results.

7.2.3 Audits of Data Quality

Battelle's Quality Manager shall audit at least 10% of the verification data acquired in the verification test. The Quality Manager traces the data from initial acquisition, through reduction and statistical comparisons, to final reporting. All calculations performed on the data undergoing audit are checked.

7.2.4 Assessment Reports

Each assessment and audit shall be documented in accordance with Section 2.9.7 of the QMP for the AMS pilot.[1] Assessment reports include the following:

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

7.2.5 Corrective Action

The Battelle Quality Manager, during the course of any audit, shall 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 is authorized to stop work.

Once the assessment report has been prepared, the Verification Testing Leader shall ensure that a response is provided for each adverse finding or potential problem and shall implement any necessary followup corrective action. The Quality Manager shall ensure that follow-up corrective action has been taken.

8 DATA ANALYSIS AND REPORTING

8.1 Data Acquisition

Data acquisition in a verification test includes recording response data from the CEMs undergoing testing, documentating sampling conditions and analytical results from the reference method, and recording operational data such as combustion source conditions, test temperatures, the times of test activities.

Data acquisition for the commercial CEMs undergoing verification shall be performed by the CEM vendors during the test. Each CEM must have some form of data acquisition device, such as a digital display whose readings can be recorded manually, a printout of analyzer response, or an electronic data recorder that stores individual analyzer readings. For all tests, the vendor shall be responsible for reporting the response of the CEM to the sample provided. The CEM data are to be provided to Battelle at the end of each test day and must include the results of all tests conducted on that day. The CEM data must include all individual readings of the CEM (i.e., TVM, EM, etc.) listed by time of day. Averaged results, e.g., TVM data averaged over the period of an OH sampling run, may also be provided, if available. If not provided, averaging shall be performed by Battelle in data processing. Electronic data files are the preferred means of data transfer, with Excel® or ASCII file formats preferred.

Other data shall be recorded in laboratory record books maintained by Battelle, EPA, and test facility staff involved in the testing. These records are reviewed on a daily basis to identify and resolve any inconsistencies. All written records must be in ink. Any corrections to notebook entries, or changes in recorded data, must be made with a single line through the original entry. The correction is then to be entered, initialed, and dated by the person making the correction.

In all cases, strict confidentiality of data from each vendor's CEM, and strict separation of data from different CEMs, is maintained. Separate files (including manual records, printouts, and/or electronic data files) are kept for each CEM. At no time during verification testing will Battelle staff engage in any comparison or discussion of different CEMs.

Table 8 summarizes the types of data to be recorded; where, how often, and by whom the recording is made; and the disposition or subsequent processing of the data. The general approach is to record all test information immediately and in a consistent format throughout all tests. Data recorded by the vendors are to be turned over to Battelle staff immediately upon completion of each test day. Identical file formats are used to make quantitative evaluations of the data from all CEMs tested to assure uniformity of data treatment. This process of data recording and compiling is overseen by the Verification Testing Leader and Battelle Quality Manager.

8.2 Data Review

Records generated in the verification test shall receive a one-over-one review within two weeks after generation, before these records are used to calculate, evaluate, or report verification results. These records may include laboratory record books, operating data from the combustion source, data from the CEMs, or reference method analytical results. This review is performed by a Battelle technical staff member involved in the verification test, but not the staff member that originally generated the record. EPA/test facility and/or vendor staff are consulted as needed to clarify any issues about the data records. The review shall be documented by the person performing the review by adding his or her initials and date to a hard copy of the record being reviewed. This hard copy is then be returned to the Battelle staff member who generated or who will be storing the record.

8.3 Reporting

The statistical data comparisons described in Sections 4.5 and 5 are conducted separately for each commercial Hg CEM. Separate verification reports are prepared, each addressing the

Table 8. Summary of Data Recording Process for the Verification Test

Data to be Recorded	Responsible Party	Where Recorded	How Often Recorded	Disposition of Data[a]
Dates, times of test events	Battelle/EPA	Laboratory record books	Start/end of test, and at each change of a test parameter.	Used to organize/check test results; manually incorporated in data spreadsheets as necessary.
Test parameters (temperature, analyte/interferant identities and concentrations, gas flows, etc.)	EPA/Test Facility/ Battelle	Laboratory record books	When set or changed, or as needed to document stability.	Used to organize/check test results, manually incorporated in data spreadsheets as necessary.
Hg CEM readings				
- digital display	Vendor	Data sheets provided by Battelle.	At specified points during each test.	Manually entered into spreadsheets
- printout	Vendor	Original to Battelle, copy to vendor.	At specified points during each test.	Manually entered into spreadsheets
- electronic output	Vendor	Data acquisition system (data logger, PC, laptop, etc.).	Continuously at specified acquisition rate throughout each test.	Electronically transferred to spreadsheets
Reference method sampling data	Test Facility/EPA	Laboratory record books	At least at start/end of reference sample, and at each change of a test parameter.	Used to organize/check test results; manually incorporated in data spreadsheets as necessary.
Reference method sample analysis, chain of custody, and results	Test Facility/EPA	Laboratory record books, data sheets, or data acquisition system, as appropriate.	Throughout sample handling and analysis process	Transferred to spreadsheets

[a] All activities subsequent to data recording are carried out by Battelle.

CEM provided by one commercial vendor. The verification report presents the test data, as well as the results of the statistical evaluation of those data.

The verification report shall briefly describe the ETV program, the AMS Center, and the procedures used in verification testing. These sections shall be common to each verification report resulting from the verification test. The results of the verification test shall then be stated quantitatively, without comparison to any other CEM tested or any comment on the acceptability of the CEM's performance. The preparation of draft verification reports, review of reports by vendors and others, revision of the reports, final approval, and distribution of the reports shall be conducted as stated in the "Generic Verification Protocol for the Advanced Monitoring Systems Pilot."[9] Preparation, approval, and use of verification statements summarizing the results of this test will also be subject to the requirements of that same protocol.

9 HEALTH AND SAFETY

All participants in the verification test (i.e., Battelle, EPA, test facility, and vendor staff) shall adhere to the test facility's health and safety requirements. Those requirements include completion of a 24-hour HAZWOPR training course before participation in any activities at the facility. Vendor staff shall operate only their Hg CEMs during the verification test. They are not responsible for operating, nor are they permitted to operate, the combustion source; they will not perform any other verification activities identified in this protocol. Operation of the CEMs themselves does not pose any known chemical, fire, mechanical, electrical, noise, or other potential hazard.

All visiting staff at the RKIS shall be given a site-specific safety briefing prior to installing and operating the CEMs. This briefing includes a description of emergency operating procedures (i.e., in case of fire, tornado, laboratory accident) and identifies and describes the location and operation of safety equipment (e.g., fire alarms, fire extinguishers, eye washes, exits). The following safe work practices must be followed by all staff involved in the Hg CEM verification at the RKIS facility:

- All staff will be required to wear protective glasses, buttoned laboratory coats, and steel-toed safety shoes while working in the facility

- Hearing protection is recommended
- Eating, drinking, and smoking are only permitted in designated areas.

A "three warning" system shall be enforced by EPA and contractor staff operating the RKIS facility to assure compliance with these safety practices:

- First infraction—violator receives a verbal warning
- Second infraction—violator receives a written warning
- Third infraction—violator will be requested to leave the facility.

Verification tests performed at other suitable locations must be carried out under the specific safety requirements of those facilities.

10 REFERENCES

1. "Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Center," U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, December 2001.

2. "Environmental Technology Verification Program Quality and Management Plan for the Pilot Period (1995-2000)," EPA-600/R-98/064, U.S. Environmental Protection Agency, Cincinnati, Ohio, May 1998.

3. "Speciated Mercury Emission Test Reports," produced in response to EPA's information collection request on utility mercury emissions, at www.epa.gov/ttn/uatw/combust/utiltox/mercury.html.

4. "Standard Test Method for Elemental, Oxidized, Particle-Bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method)," American Society for Testing and Materials, Draft Method, October 27, 1999.

5. Personal communication from Jeff Ryan, U.S. EPA/ORD/NRMRL, June 28, 2000.

6. "Evaluation of Flue Gas Mercury Speciation Methods," EPRI Technical Report TR-108988, Electric Power Research Institute, Palo Alto, California, December 1997.

7. "Proposed Performance Specification 12 for Total Mercury Emission Monitoring Systems," U.S. Environmental Protection Agency, Washington, D.C., April 19, 1996.

8. "Field Evaluation of MERCEM Mercury Emission Analyzer System at the Oak Ridge TSCA Incinerator," East Tennessee Technology Park, Oak Ridge, Tennessee, Report BJC/OR-374, prepared for the U.S. Department of Energy by Bechtel Jacobs Company LLC, March 2000.

9. "Generic Verification Protocol for the Advanced Monitoring Systems Pilot," U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, October 1998.