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Environmental Technology Verification Program

Advanced Monitoring Systems Center

Test/QA Plan for Pilot-Scale Verification of Continuous Emission Monitors for Mercury

ETV ETV ETV

TEST/QA PLAN

FOR

PILOT-SCALE VERIFICATION OF CONTINUOUS EMISSION MONITORS FOR MERCURY

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Prepared by

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1.0 INTRODUCTION

1.1 Test Description

This test/quality assurance (QA) plan provides detailed procedures for a verification test of continuous emission monitors (CEMs) used to measure total and chemically speciated mercury (Hg) in source emissions. The verification test will be conducted under the auspices of the U.S. Environmental Protection Agency's (EPA) Environmental Technology Verification (ETV) program. The purpose of ETV is to provide objective and quality assured performance data on environmental technologies, so that users, developers, regulators, and consultants have an independent and credible assessment of what they are buying and permitting.

The verification test will be performed by Battelle, of Columbus, OH, 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 the verification test, Battelle will follow procedures specified in this test/QA plan, and will comply with quality requirements in the "Quality Management Plan for the ETV Advanced Monitoring Systems Pilot" (QMP).[1]

1.2 Test Objective

The objective of the verification test is to quantify the performance of commercial mercury CEMs, by comparison to reference Hg measurements, 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 test/QA plan, is planned to assess performance at a full-scale facility.

1.3 Organization and Responsibilities

The verification test will be performed by Battelle in cooperation with EPA and the vendors who will be having their analyzers verified. The organization chart in Figure 1 shows the individuals from Battelle, the vendor companies, and EPA who will have responsibilities in the verification test. The specific responsibilities of these individuals are detailed in the following paragraphs.

1.3.1 Battelle

Dr. Thomas J. Kelly is the AMS Center's Verification Testing Leader. In this role, Dr. Kelly will have overall responsibility for ensuring that the technical, schedule, and cost goals established for the verification test are met. More specifically, Dr. Kelly will:

- Coordinate Battelle, EPA, contractor, and vendor staff to conduct the verification test
- Guide the Battelle/EPA/contractor/vendor team in performing the verification test in accordance with this test/QA plan
- Have overall responsibility for ensuring that this test/QA plan is followed.
- Prepare the 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
- 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 the effort to ensure that budget is not exceeded
- Ensure that confidentiality of vendor information is maintained.

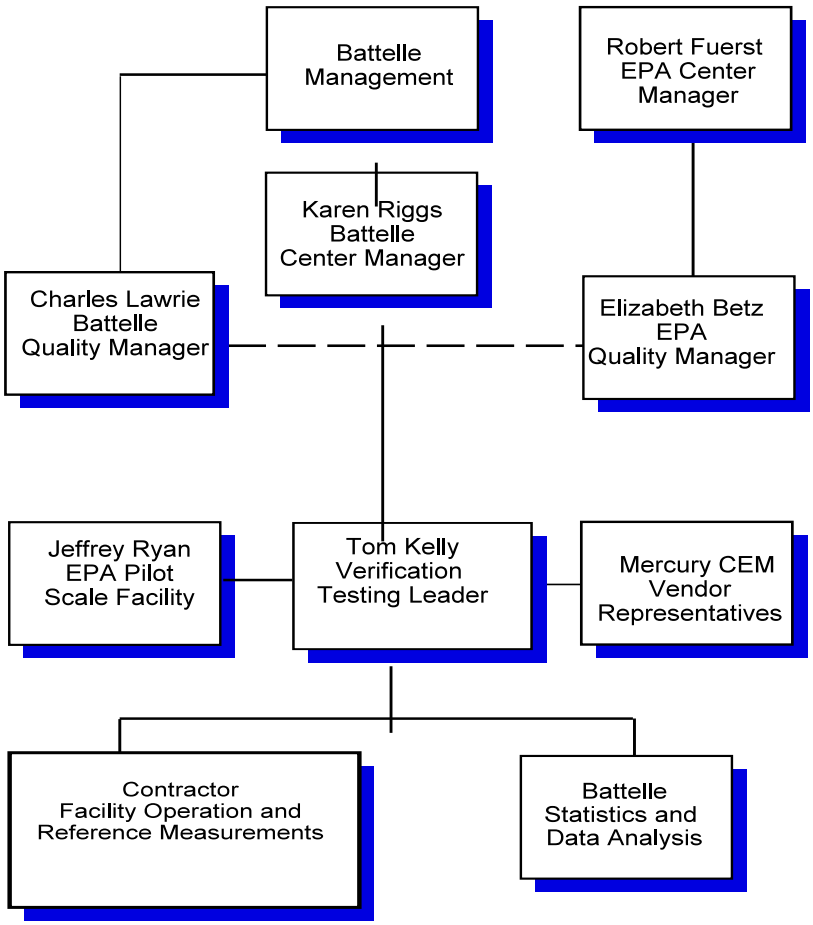

Figure 1. Organization Chart for the Verification Test

Ms. Karen Riggs is Battelle's AMS Center manager. As such, Ms. Riggs will:

- Review the draft test/QA plan
- Review the draft verification reports and statements
- Coordinate distribution of final test/QA plan, 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 Dr. Kelly in responding to any issues raised in assessment reports and audits
- Maintain communication with EPA's Center Manager.

Mr. Charles Lawrie is Battelle's Quality Manager for the AMS Center. As such, Mr. Lawrie will:

- Review the draft test/QA plan
- Maintain communication with EPA's Quality Manager for the AMS Center
- Conduct a technical systems audit once during the verification test
- Review results of performance evaluation audit(s) specified in this 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 internal audits indicate that data quality is being compromised; notify Battelle's AMS Center Manager if such an order is issued
- Provide a summary of the QA/QC 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 of Battelle's Statistics and Data Analysis Systems (SDAS) department will provide statistics and data analysis support. In particular, SDAS staff will:

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

Staff of Battelle's Atmospheric Science and Applied Technology (ASAT) department will support Dr. Kelly in planning and conducting the verification test. These staff will:

- Assist in planning for the test, and making arrangements for the installation of 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 this test/QA plan

1.3.2 Vendors

Vendor representatives will:

- 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 CEM throughout the verification test
- Participate in verification testing, including providing data acquisition for their mercury CEMs
- Provide to Battelle staff the data from their CEM at the conclusion of each test day
- Review their respective draft verification report and verification statement.

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)" (QAMP).[2] The roles of specific EPA staff under the QAMP are as follows:

Ms. Elizabeth Betz is EPA's Quality Manager. For the verification test, Ms. Betz will:

- Review the draft test/QA plan
- Perform, at her option, one external technical systems audit during the verification test
- Notify the Battelle AMS Center's 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 the external audit, if one is performed
- Review the draft verification reports and statements.

Mr. Robert Fuerst is EPA's AMS Center Manager. As such, Mr. Fuerst will:

- Review the draft test/QA plan

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

This verification test will be conducted in collaboration with Jeffrey Ryan of EPA's Office of Research and Development, National Risk Management Research Laboratory (ORD/NRMRL). Mr. Ryan's responsibilities are:

- 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 vendors' 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 facility operations.
- Review draft verification reports and verification statements.

1.3.4 Contractor

The RKIS Facility is operated for EPA by an on-site contractor (Arcadis/Geraghty and Miller). This contractor will perform some duties under contract with EPA, and additional duties related to the verification test under a subcontract with Battelle. The contractor's responsibilities will be:

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 quality assurance results to Battelle in an agreed-upon format
- Provide input on facility operating conditions and procedures for the verification test report

- Support Dr. Kelly in responding to any issues raised in assessment reports and audits related to facility operation.

2.0 APPLICABILITY

2.1 Subject

This test/QA plan is applicable to the verification testing of commercial continuous emission monitors for determining total and/or chemically speciated mercury in combustion source emissions. Total mercury is the sum of mercury in all phases and chemical forms in the combustion gas, including elemental mercury (Hg^o) and oxidized mercury (primarily mercuric chloride ($HgCl_2$) and mercuric oxide (HgO)) vapors, and particulate-phase mercury. Most commercial mercury CEMs do not measure the particulate phase mercury; instead they filter out particulate matter, and measure the total of the vapor-phase mercury species. This approach is taken because at least for electrical generating facilities, recent stack test results indicate that the great majority of emitted mercury 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 commonly accomplished by a difference measurement, in which oxidized mercury is intermittently chemically reduced or thermally decomposed to elemental mercury for detection.

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

The terminology to be used in this test/QA plan is as follows:

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

The CEMs tested according to this plan will be verified for their measurement of any and all of the applicable mercury components listed above. For example, a monitor that determines TVM and EM, and by difference determines OM, will be verified for measurements of all three components. In the U.S., emission regulations on combustion sources are expected to address only total mercury. However, there are valuable non-regulatory uses of mercury 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 test/QA plan, 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 mercury 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 mercury 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 test/QA plan calls for the use of a natural gas fired pilot-scale combustion 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, such as an

incinerator, may also be used, provided they allow appropriate control of test conditions and mercury levels.

2.2 Scope

The overall objective of the verification test described in this plan is to provide quantitative verification of the performance of the mercury CEMs in realistic test conditions. Since mercury 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 designated as PS-12,[7] as a proposed description of how to assess the acceptability of a mercury 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 which are inappropriate or currently not feasible. For example, the draft PS-12 calls for the CEM to be able to measure both vapor and particulate phase mercury. As noted above, most current CEMs do not determine particulate-phase mercury. Also, the draft PS-12 calls for the use of absolute standards for both EM and OM (the latter in the form of $HgCl_2$). Although elemental mercury 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 instrumental drift and precision,[e.g.,8] but their absolute quantitation may not be sufficient to assess instrumental 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 simply adopt PS-12 procedures as the basis for this verification test. Instead, this test is 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/QA plan 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) will 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 will be assessed for EM only, using commercial compressed gas standards of EM. Interference response will be assessed in sampling of the combustion facility flue gas, rather than in sampling of diluted calibration gases, as called for in PS-12. Calibration error will not be assessed in this test, because of the absence of absolute standards.

It is beyond the scope of this verification test to simulate the aging and exposures that may affect a CEM during routine long-term use. This verification test evaluates the performance of new CEMs, installed in a pilot-scale facility, over a relatively short test period, in the hands of vendor staff skilled in their operation. 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 will be documented, and the amount of time each CEM is operational over the verification test period will be recorded, to assess data completeness.

3.0 SITE DESCRIPTION

This verification test will be conducted at the Rotary Kiln Incinerator Simulator (RKIS) at the EPA Incineration Research Laboratory in Research Triangle Park (RTP), North Carolina. This section of the test/QA plan 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 3-1. The RKIS was modified in 1997, for a simultaneous test of eight multi-metals CEMs; Figure 2 and Table 3-1 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 and the afterburner.

Combustion flue gases exiting the afterburner are rapidly cooled to approximately 540°C (1000°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 via an air dilution damper just upstream of a 9.9 m (35 ft) long, 20.3 cm (8 in) diameter duct which 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 (NPT) 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 port

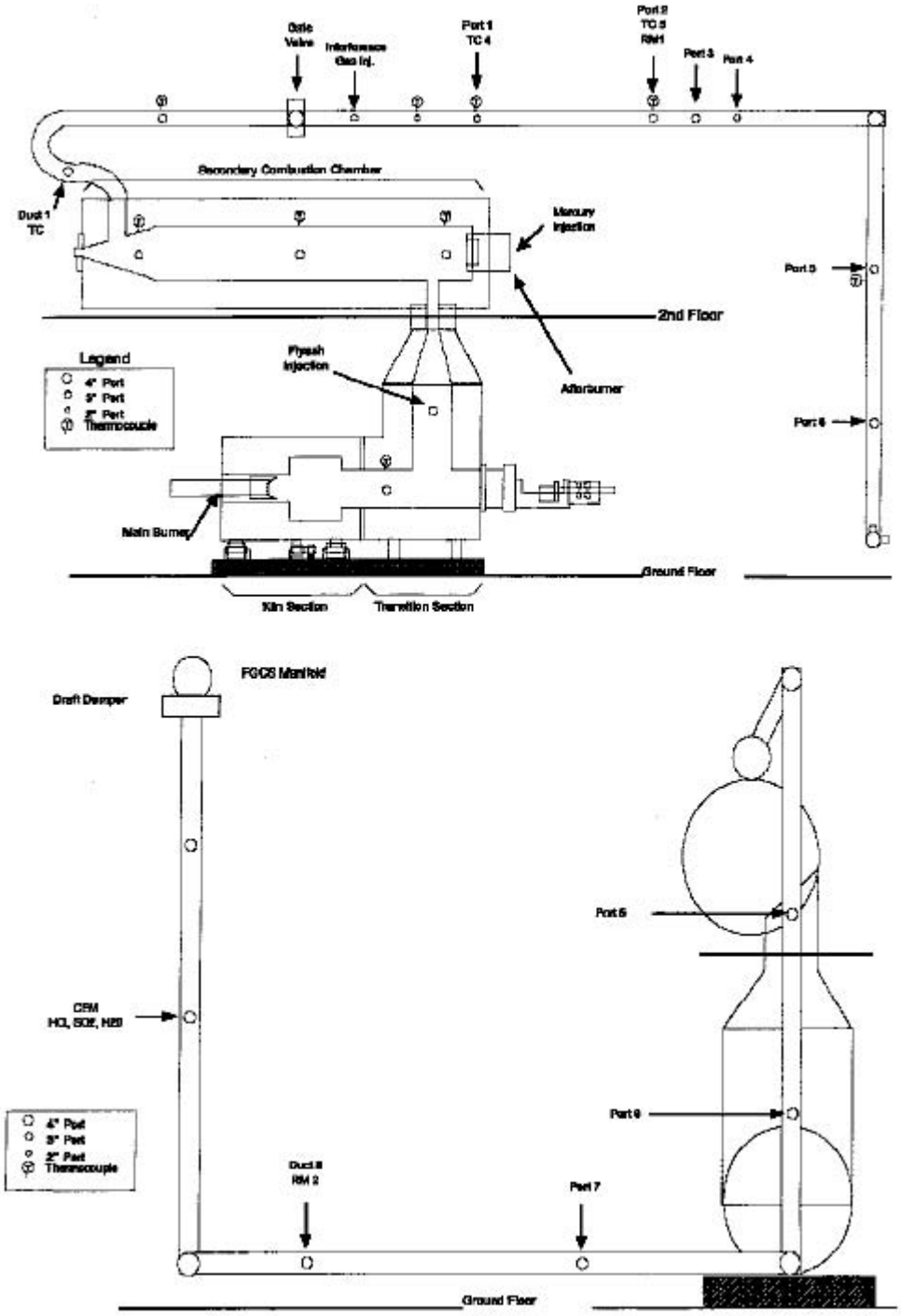

Figure 2. Side View (top) and End View (bottom) of the RKIS Test Facility

Table 3-1. 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)

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 located 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 intervals of about two meters 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 continuous emission monitors 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 3-2, 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 provide verification 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 Hg 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 percent by volume. The duct is at a negative pressure (draft) of nominally 0.25 kPa (- 1 inch 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 will have two major roles in this verification test. First, measurements of major diluent gases in the flue gas (O_2, CO_2) will be used, along with H_2O content results obtained from the Ontario Hydro 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) will be 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 will be 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 will be NO; typically 5 to 10 percent of the injected NO will be converted to NO_2 in the RKIS. HCl levels may be prepared by injection of HCl gas, or of chlorine gas (Cl_2), and will be monitored with the RKIS CEM for HCl. Injection of 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 will be 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 3-2. 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 will be fired with natural gas. No waste or simulated waste feed to the kiln will be employed, however mercury will be introduced into the flue gas by atomizing an aqueous solution of mercuric nitrate ($Hg(NO_3)_2$) into the afterburner. The mercury solution will be atomized into an annulus inside the afterburner natural gas feed tube. The solution will be atomized at the exit from that annulus, introducing Hg-containing aerosol droplets directly into the burner flame. The droplets will evaporate rapidly in the flame

zone, yielding primarily dry, vapor-phase mercury. The oxidation state of the mercury will be manipulated by also introducing gaseous chlorine into the RKIS.

Two different mercury solutions will be used in the test, to produce both 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 nominally10 mL/min. The high concentration solution will be diluted approximately ten-fold to make the solution for the lower target concentration tests. The target low and high mercury concentrations are about 8 $\mu g/m^3$ and 80 $\mu g/m^3$, respectively.

Particulate matter will also be 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 for the verification of TM and PM measurement capabilities of any CEMs that determine the PM component. A K-Tron mass-controlled feeder will be used to inject coal fly ash from a utility boiler directly into the hot flue gas as it exits the kiln. The fly ash to be used was selected for its low reactivity with vapor-phase mercury, and will be thoroughly characterized for mercury content. The particulate loading during verification testing will be determined using the filter and front half catch from the Ontario Hydro reference method trains, rather than from a separate Method 5 train. One Ontario Hydro train from each of the two reference sampling locations will be used for particulate loading determination in each run.

In addition to mercury and particulate matter, other common flue gas constituents will be introduced, for simulation of flue gas composition, and for evaluation of potential interferences in Hg CEM measurements. Specifically, Cl_2, HCl, CO, SO_2, and NO will be introduced by dilution of compressed gases into the flue gas.

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

4.0 EXPERIMENTAL DESIGN

4.1 General Design

The verification test described in this test/QA plan will be conducted over about a three-week period, at the RKIS facility. The first week will be spent installing the commercial CEMs at the RKIS, and conducting a shakedown run of all systems before the verification effort begins. Testing will not begin until all the reference method equipment and RKIS 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, it will be required that all participating CEMs arrive at the facility by a specified day, and be ready to begin testing within one week after arrival, or when the RKIS facility itself is fully ready, whichever is later. CEMs which are not operational at that time may join the testing process once they come on line.

The two weeks of testing will follow immediately after the setup/shakedown period. A similar test schedule will be followed in each of the two weeks, but the Hg levels and the levels of other flue gas constituents will be different in the two weeks. Verification will involve comparisons of the CEM results with those from a time-integrated reference method (the Ontario Hydro Method),[4] as well as challenges with interferences and with Hg^o compressed gas standards. In general, different test activities will be conducted on different days, but certain test procedures will take place on every test day. All participating CEMs, and the reference method sampling trains, will sample flue gas at the same time from the RKIS duct. However, it will not be possible to co-locate 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 will be collected at both the upstream and downstream end of the duct in all verification testing, to document the mercury levels and mercury 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 mercury 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 will be 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 will be 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 will not be 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 will follow the weekly schedule shown in Table 4-1. 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

Table 4-1. 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.

days. A day for maintenance and a scheduled down day complete the week. As Table 4-1 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 will be carried out in the morning, resulting in a series of five successive days for this test. On Friday morning, a sampling system bias test will also be conducted, in which the Hg^o standard gas will first be 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 will be tested, using the Hg° standard gas. The afternoon of Thursday will be devoted to testing of interferences in the flue gas matrix, and part of the afternoon of Friday will be used to perform a qualitative test of the CEMs' ability to monitor Hg at levels below 5 $\mu g/m^3$. The rest of Friday afternoon will be available to repeat tests from earlier days, and to address any unforseen problems or opportunities in sampling. Saturday of the first week will be used to prepare for the next week of testing, or to maintain the RKIS or other systems.

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

The interference testing will be conducted by establishing a stable mercury 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 will be assessed by comparing the CEM response with only Hg added, to the response when Hg and one or more interferants are added. The Hg level used in this test will be the 8 $\mu g/m^3$ level to be used in the first week of verification testing. The interferant levels used will be relatively high values to assure a definite conclusion about the presence or absence of an interference.

4.3 Test Conditions

Table 4-2 shows the approximate levels of mercury and other constituents that will 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 is chosen so that the lower mercury concentration is used first, to avoid contaminating the RKIS during testing. The

approximate levels shown in Table 4-1 will be maintained throughout all periods of Hg addition and reference method sampling. It is expected based on past experience at the RKIS that the flue gas levels of all constituents in Table 4-2 will be maintained within10 percent of the target levels shown.

Table 4-2. Summary of Flue Gas Constituent Concentrations Planned for Use in Verification Testing

Test Week	Hg (µg/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 will be held constant throughout the entire sampling period. The intent of this approach is to allow comparisons of CEM data to reference method data under constant conditions. Higher levels of flue gas constituents will be used in the interference testing, as described in the next section.

4.4 Test Procedures

The RKIS will be operated continuously during the entire test period, and will not be shut down overnight. Such continuous operation is intended to minimize the potential for retention and subsequent release of mercury by the refractory or other components of the RKIS. The Hg CEMs undergoing verification will be 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 will be performed by contractor staff. The sampling ports will be 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 will be supplied (one at a time) with zero gas and then with a commercial compressed gas standard containing elemental mercury. The response to each gas will be recorded on each test day to assess the zero and calibration drift of the CEMs. In this test, the mercury standard will be used solely as a stable, clean sample matrix, not as an absolute mercury standard. On one test day in the first week of testing, the rise and fall times of the CEMs will be 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 will be delivered first directly to the CEM's mercury analyzer, and then through the CEM's sample interface, to assess bias introduced by the interface itself.

During performance of the drift checks, the reference method sampling trains will be assembled and leak checked, and the RKIS combustion gas CEMs will be calibrated in accordance with facility standard operating procedures. At this time, the RKIS operation will be 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 mercury spike solution to give the day's target flue gas concentration will be initiated. Mercury solution will be fed to the RKIS for at least 30 min before reference method sample initiation. The addition of the other flue gas constituents will follow this same procedure. The mercury CEMs will begin recording data as soon as they are brought on-line. However, the reference method sampling will start no sooner than a time previously agreed upon with the CEM vendors. The CEM vendors will be given at least 15 minutes notice prior to initiation of reference method sampling.

The number of reference method samples collected will depend on the target mercury concentration. The reference method sampling time will 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 will allow two reference method samples per day (6 per week) in the first week of testing, and three per day (9 per week) in the second week. During verification testing, sampling will be conducted simultaneously with four trains of the OH method, two each at the upstream and the downstream end of the RKIS duct. Thus each of the two or three measurement periods during a test day will provide four OH results for

comparison to the CEM data. To ensure that the reference method and CEM data sets are indeed parallel and comparable for each period, the CEM vendors will 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 will 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 will also sample at a single point in the center of the duct, non-isokinetically. Each CEM will operate 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 will be approximately 250°F, sufficient to keep the sample gas above its dew point; no attempt will be made to maintain the sample gas at its stack temperature. An EPA Method 2 traverse will be done at each reference sampling location before OH sampling, and again after OH sampling. The pre-run traverse will be used to set the isokinetic sampling rate. The average of the pre- and post-sampling traverses will be used for final calculations.

The chemical analysis of recovered sample fractions from OH method trains will 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 will 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 will be stored under refrigeration until transfer to the analytical laboratory. Unique sample identification numbers will be implemented so that final data used for verification can be traced back through the analytical process to the original sample. Field blank samples will also be recovered from one blank sampling train on each day that OH method samples are collected. Before sample recovery, that blank train will be transported to the upstream or downstream sampling location at the RKIS on alternate days. Care will 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 4-1) is illustrated in Figure 3. That figure shows the schedule for a day in the first week of testing when

two 3-hour Ontario Hydro runs are conducted. In the second week, three 1-hour runs will be conducted each day. The test day begins with a challenge of each CEM using zero gas and a commercial standard gas of Hg°. Two different standard cylinders will be used, of equal concentrations. One group of the CEMs undergoing testing will always be tested with Hg° standard cylinder #1, and the remaining CEMs will be challenged with Hg° standard cylinder #2. The two groups of CEMs will be chosen so that standard gas consumption by the two groups is approximately equal. This parallel approach will allow testing with the Hg° standards to proceed efficiently, while assuring that sufficient Hg° standard gas is available to complete the week of testing.

Following the completion of the Hg° standard gas test, introduction of Hg, SO_2, particulate matter, etc., to the RKIS will begin. As shown in Figure 3, introduction of these species into the RKIS will begin at least 30 minutes before the start of the first OH run, and will continue until the last OH run is completed. The flue gas composition will be maintained in this period at the levels shown in Table 4-2.

The daily schedule of the test day on which interference tests are done (Thursday in Table 4-1) is shown in Figure 4. The same Hg° standard gas challenges will be done in the morning as described above in the context of Figure 3. Then a stable Hg level will be introduced into the RKIS, and the response of the CEMs being tested will be allowed to stabilize. Then each of several potential interferants will also be 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 4-3. After the last individual interferant (Cl_2) has been tested alone, the Cl_2 addition will be continued, and the NO addition will be resumed, to assess whether the combination of NO_x and Cl_2 produces an interference. Subsequently, the other gases (SO_2, CO, HCl) will also be injected, to produce a mixture of all five interferants at the concentrations

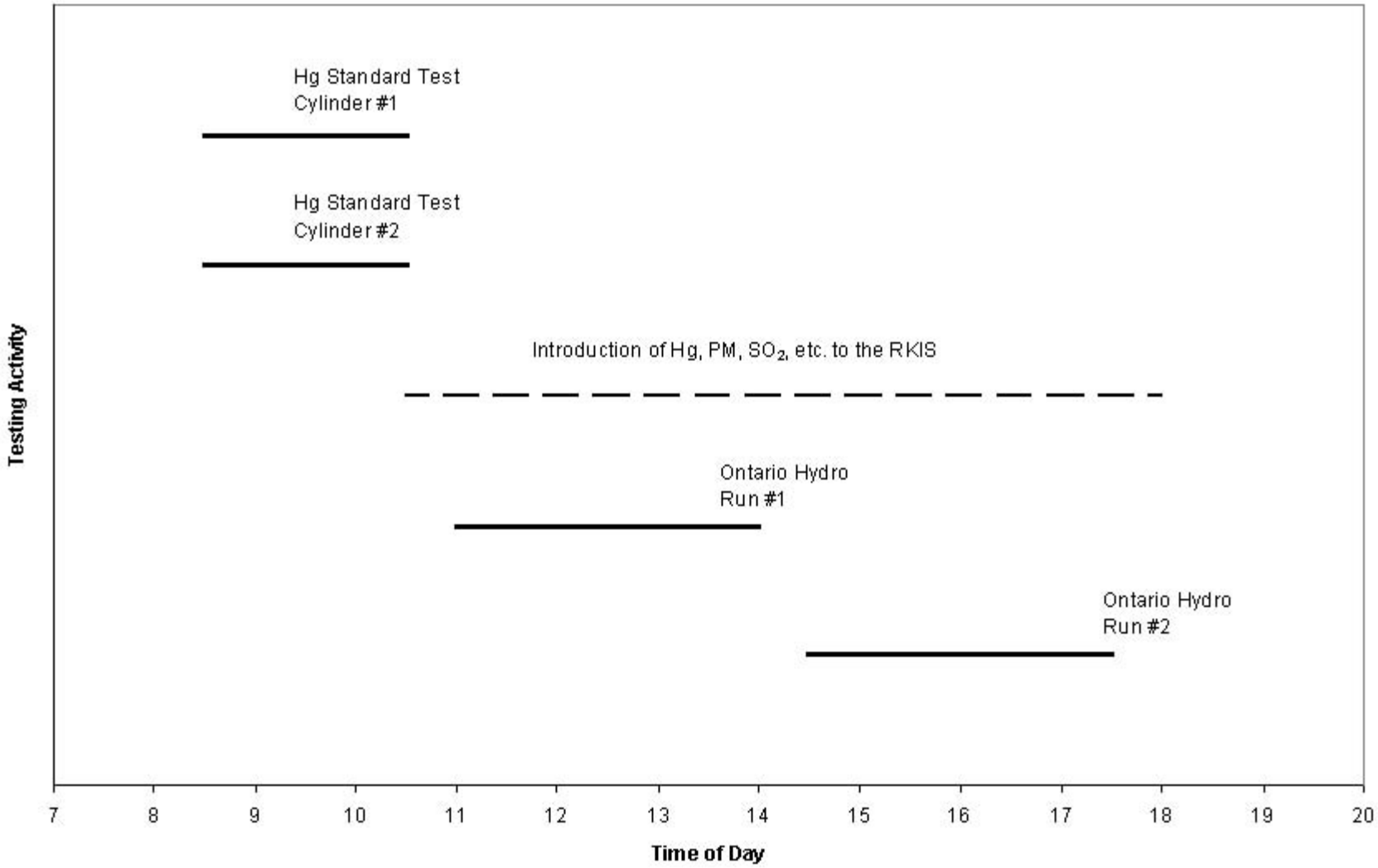

Figure 3. Schedule of Verification Test Day with Ontario Hydro Sampling

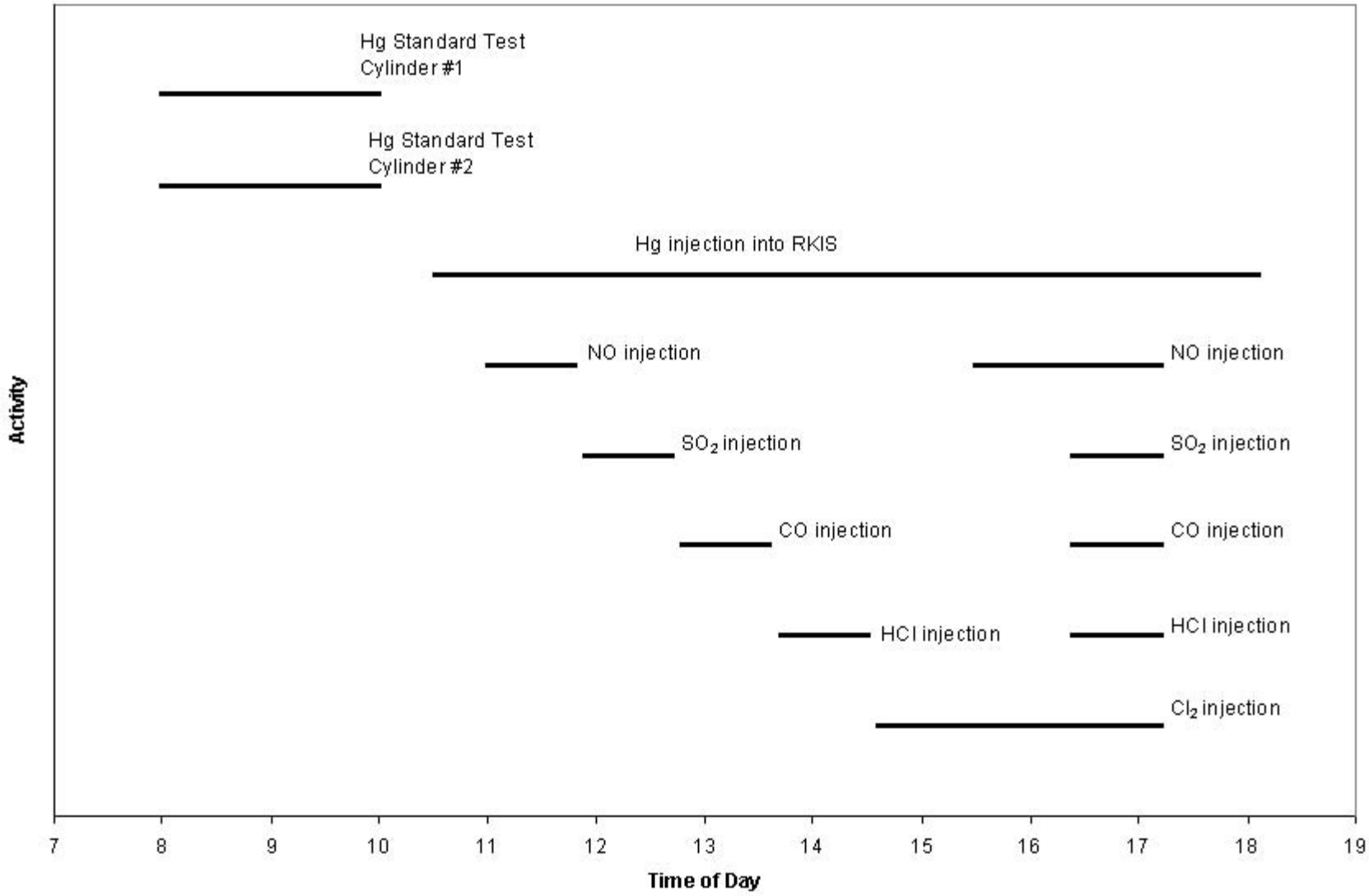

Figure 4. Schedule of Interference Test Day

Table 4-3. 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

shown in Table 4-3. Finally, all the interferants will be shut off, and measurements will be made again with only the Hg injection taking place. Throughout the test, the Hg injection will be held constant, and the Hg CEM responses in the presence of interferants will be compared to those with only Hg injected into the RKIS.

A final test will assess qualitatively the ability of the Hg CEMs to measure Hg levels below 5 $\mu g/m^3$. This test will be conducted on Friday of the first test week (Table 4-1), by starting with no Hg injection, then establishing a 1 $\mu g/m^3$ Hg level, and then increasing the Hg concentration in successive steps of two, i.e., to 2 $\mu g/m^3$, then to 4 $\mu g/m^3$, then to 8 $\mu g/m^3$. The Ontario Hydro method does not provide good precision at these low levels, so no absolute comparison of methods will be made. However, the rate of introduction of Hg to the RKIS can be easily and accurately changed, and provides a valuable test of Hg detection. This test will be 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 will be compared to that with no Hg addition, and the lowest Hg level producing a positive response will be reported. The remainder of the test day after completion of the low level Hg test will be used to repeat or finish other test activities as necessary, as indicated in Table 4-1.

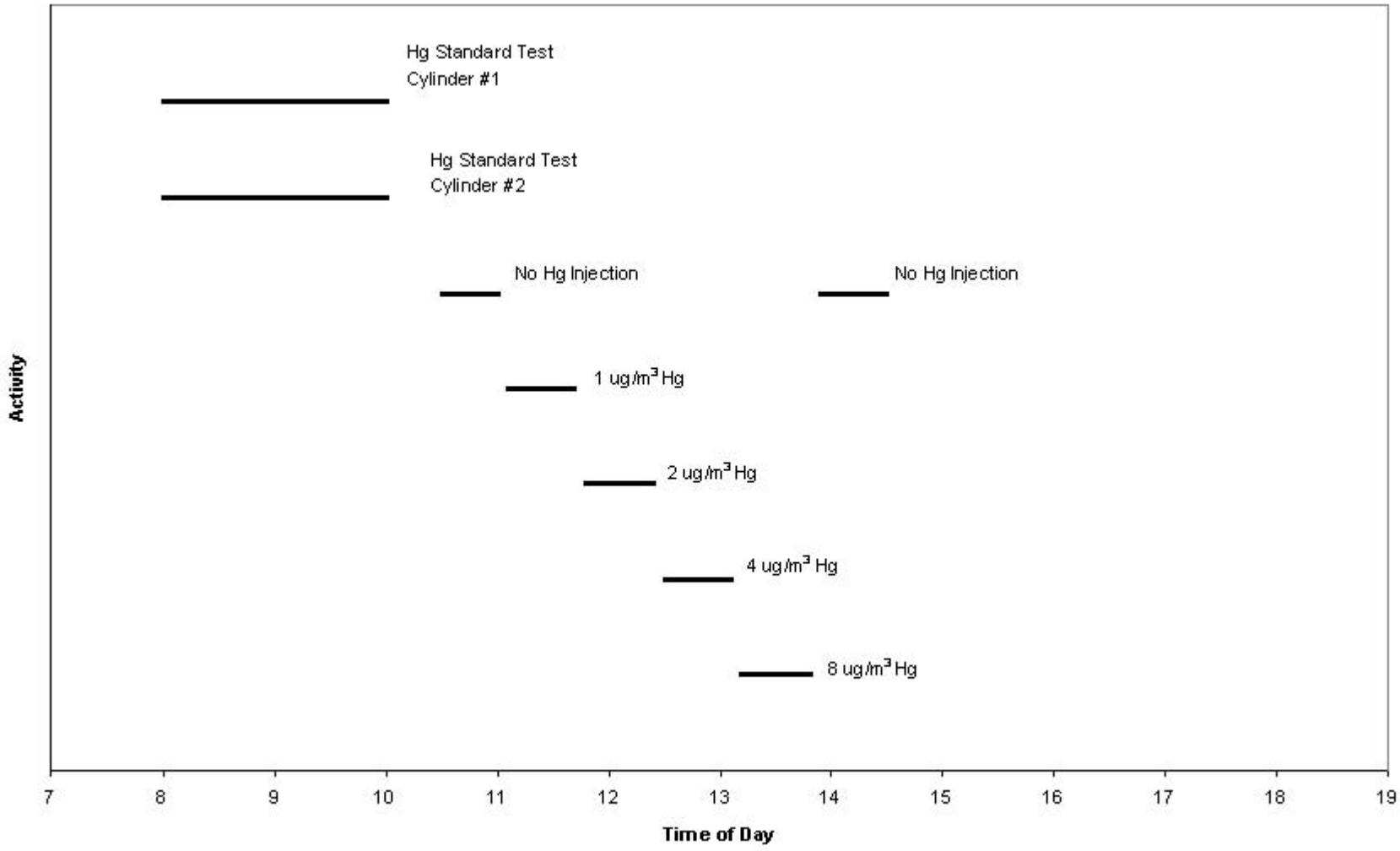

Figure 5. Schedule for Low-Level Hg Detection Test

4.5 Data Comparisons

This section describes how the reference and CEM data will be used and compared to quantify the performance of the CEMs. Table 4-4 summarizes the data that will be used for the verification comparisons.

Relative accuracy will 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 mercury, then only the TVM results from the Ontario Hydro method will be used for verification. However, if the CEM also measures oxidized, elemental, or particulate mercury, then those results from the Ontario Hydro method will also be used for verification. A total of 15 Ontario Hydro sampling runs is planned in the verification test (6 with lower Hg levels, and 9 with higher Hg levels), with four Ontario Hydro sampling trains operating simultaneously in each period. Thus a total of 60 Ontario Hydro samples will be used to evaluate relative accuracy.

The purpose of sampling with dual Ontario Hydro 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 mercury concentrations to be used in this verification, it is expected from previous results that the precision of duplicate Ontario Hydro results will be within about 10 percent. 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 mercury levels, will also 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, will be considered in screening for reference data quality. The Ontario Hydro results will be reviewed before verification comparisons are made, to identify individual outliers from the full set of reference method results. That is, the Ontario Hydro results will be screened for three factors:

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

Table 4-4. 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 Ontario Hydro 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 Ontario Hydro 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, 1, 2, 4, and 8 $\mu g/m^3$ Hg levels.

Ontario Hydro test results which are identified as outliers on any of these criteria will be 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 will be 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, effort will be made to find an assignable cause for the divergent result.

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

Precision of the CEMs will be assessed based on the individual measurements performed by each CEM over the duration of each Ontario Hydro method sampling run. For example, if a CEM provides an updated measurement every 5 minutes, then over a one-hour sampling run a total of 12 readings would be obtained. The average and standard deviation of those readings will be calculated to assess precision. This procedure will be applied to all 15 of the Ontario Hydro method sampling intervals.

Calibration and zero drift will 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 will be used to assess zero drift, and an equal number to assess calibration drift. Note that only the relative stability of the response will be assessed, i.e., the Hg^o standard will not be used as an absolute calibration standard. The sampling system bias test will be performed once as part of the calibration/zero drift test procedure, in each week of testing.

Interference effects will be assessed by adding potential interferants one at a time during a constant addition of mercury to the RKIS flue gas, and comparing the CEM readings with and without the interferant. This will be done only in the first week of testing (i.e., at the lower mercury level), for the seven individual interferants or combination of interferants described in Section 4.4. Thus a total of seven comparisons will be made of interference effects.

CEM response times will be determined by recording successive CEM readings at times when mercury delivery to the CEM is started or stopped. This procedure will be 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 will be determined, resulting in two determinations of rise time and two of fall time.

Low level Hg response will 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 will be reported.

No additional test activities will be required to determine the data completeness achieved by the CEMs. Data completeness will 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 will 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.

5.0 STATISTICAL CALCULATIONS

This 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 (RA) of the CEMs with respect to the reference (Ontario Hydro) method will be assessed by:

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

where d refers to the difference between the Ontario Hydro and CEM results, and x corresponds to the Ontario Hydro 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 will be determined for an α value of 0.025 (i.e., 97.5 percent confidence level, one-tailed). The RA 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 will be calculated separately for the first and second week of testing, with up to 24 samples and up to 36 samples, respectively (assuming all Ontario Hydro method samples can be treated as independent results). With these numbers of samples, the RA procedure stated in PS-12[6] will be followed, i.e., up to three results may be omitted from the RA calculation. The impact of the number of data points (n) on the RA value will be noted in the verification report. Relative accuracy will 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 will be assessed in terms of the coefficient of determination (r^2), which is the square of the correlation coefficient (r). The coefficient of determination will be calculated for each parameter measured by each CEM (i.e, TVM, EM, OM, etc.). This calculation will be made separately for the first and second week of testing, with up to 24 samples and up to 36 samples, respectively (assuming all Ontario Hydro method samples can be treated as independent results).

5.3 Precision

Precision will be calculated in terms of the percent relative standard deviation (RSD) 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 Ontario Hydro method sampling run, all readings from a CEM undergoing testing will be recorded, and the mean and standard deviation of those readings will be calculated. Precision (*P*) will then be 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 will be performed for each parameter measured by the CEM (i.e., TM, EM, OM, etc.). This calculation will be done for each CEM, using data from every Ontario Hydro method sampling run (15 in all). The verification report will note that the calculated precision is subject to the variability of the test facility, not only the CEM variability. However, since precision will be 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 will be made, all CEM data from the periods of precision testing will 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 will be noted in all verification reports.

5.4 Calibration and Zero Drift

Calibration and zero drift will be 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, will be used for this calculation, in each of the two weeks of verification testing. The relative standard deviation (RSD) will be calculated as

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

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, will indicate the day-to-day variation in zero and standard readings.

5.5 Sampling System Bias

Sampling system bias will 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,

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

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 will be determined during sampling of combustion flue gas, in terms of the difference in response to a constant mercury level when a single interferant is added or removed. Interferences will be 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 will be determined as the time after a step change in mercury concentration when the CEM reading has reached a level equal to 95 percent of that step change. Both rise time and fall time will be determined. CEM response times will be 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 will require 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 will be assessed by comparing responses at successive levels of 0, 1, 2, 4, 8, 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 will be reported. The data from all CEMs will be reviewed collectively, to indicate whether absence of a response may be due to the limitations of the Hg injection process, or to limitations of CEM response. For example, if no CEM shows a response at the 1 $\mu g/m^3$ level, then no conclusion will be drawn about detection of that level, since inadequate injection rather than lack of detection may be the cause.

6.0 MATERIALS AND EQUIPMENT

6.1 Gases and Chemicals

6.1.2 Interference Gases

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

6.1.3 High Purity Nitrogen/Air

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

6.1.4 Mercury Standard Gases

Two compressed gas standards containing elemental Hg will be obtained from Spectra Gases for use in assessing drift of the CEMs. These will 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 will be obtained, if required to meet the gas consumption rates of the CEMs during the test. Each Hg°standard cylinder will be analyzed both before and after the verification test, by sampling the cylinder contents with EPA Method 101A and analyzing for mercury. That analysis will be done by the University of North Dakota, Energy and Environmental Research Laboratory (EERC).

6.1.5 Injection Mercury Solutions

The mercury solutions used to introduce mercury into the primary combustion zone of the RKIS will be made from commercial ACS reagent grade mercury (II) nitrate monohydrate (minimum 98% purity), using deionized water. A measured mass of the reagent is dissolved in deionized water with 25 ml concentrated nitric acid (70 wt. percent, ACS reagent grade), and

diluted to 4 L 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 ml of the nitric acid, in deionized water, up to a 4 L 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 will be determined by the OH method sampling, and not by calculation of the injected Hg. Solutions will be made up only as needed for injection into the RKIS, to minimize waste. All stock and injection solutions will be prepared under the direction of Jeff Ryan of EPA.

6.1.6 Mercury Spiking Standard

A NIST-traceable aqueous Hg standard, obtained from a commercial supplier, will be used as the spiking solution in the performance evaluation of Ontario Hydro analysis noted in Section 7.2.2. If spiking of the particle filter in the Ontario Hydro train is required, as a performance evaluation in verifying CEM determinations of particulate Hg, then a NIST coal fly ash standard reference material will be used as the spiking material.

6.2 Reference Method

6.2.1 Sampling Trains

The glassware, filters, and associated equipment for performance of the Ontario Hydro reference method[4] sampling will be supplied by EPA at the RKIS facility. Multiple trains will be supplied so that as many as twelve 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 will be the responsibility of the contractor in this verification test.

6.2.2 Analysis Equipment

Laboratory equipment for sample recovery and analysis will be provided by the laboratory contractor. This will include all chemicals and solutions for rinsing train components and recovering impinger samples, as well as cold vapor atomic absorption (CVAA) or atomic fluorescence (CVAFS) spectroscopy equipment for mercury determination.

6.3 RKIS Monitoring Equipment

This verification will make use of monitoring equipment already integrated into 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 3-2. These devices are considered part of the RKIS facility for purposes of this test, and will be operated during this verification according to normal RKIS procedures.

6.4 Equipment Used for Performance Evaluation Audits

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

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

These devices will 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 will be used, to audit the balance used to weigh impingers from the OH trains, for determining flue gas H_2O content.

7.0 QUALITY ASSURANCE/QUALITY CONTROL

7.1 Equipment Calibrations

7.1.1 RKIS Monitoring Equipment

The RKIS CEMs and other monitoring devices noted in Section 6.3 will be calibrated by EPA and RKIS contractor staff according to normal facility procedures. However, a distinction must be made between those measurements which factor directly into verification results, and those which are secondary in nature.

Measurements which factor directly into verification results are those that are used in calculation of results from the Ontario Hydro method. Those include flue gas temperature, pressure, and O_2 and CO_2 content. For these measurements, compliance level calibration procedures are required, and will be carried out by EPA and/or RKIS contractor staff. The pertinent calibration procedures will be conducted on a schedule chosen by these 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 will be determined from impinger weights in the Ontario Hydro trains. Calibration records for the balance used will be documented.

Measurements which do not factor directly into verification results include monitoring of the pollutant gases CO, NO_x, SO_2, and HCl. These data will 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, though 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, will be sufficient.

7.1.2 Reference Method

The contractors performing the Ontario Hydro method sampling must perform all required quality assurance/quality control (QA/QC) activities stated in the method. This includes

provision of blank sampling trains (one per sampling day, at either the upstream or downstream location), and of blank sampling materials (filters, reagent solution blanks) in the field. Documentation of these activities will be required for inclusion in the verification data file. Deviation from the Ontario Hydro method[4] will occur only in that traversing of the duct will not be done. Options for making particulate mass measurements, and for quickly turning glassware around in sample recovery, will be used. Spiking of Ontario Hydro trains, as recommended in the method[4] will be performed by Battelle staff, as described in Section 7.2.3.

7.1.3 Analytical Laboratory

The laboratory conducting the analysis of samples from the Ontario Hydro method must provide documentation of 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 Assessment and Audits

7.2.1 Technical Systems Audits

Battelle's Quality Manager, Mr. Charles Lawrie, will perform a technical systems audit (TSA) once during the performance of this verification test. The purpose of this TSA is to ensure that the verification test is being performed in accordance with this test/QA plan and that all QA/QC procedures are being implemented. In this audit, Mr. Lawrie may review the reference sampling and analysis methods used, compare actual test procedures to those specified in this plan, and review data acquisition and handling procedures. Mr. Lawrie will 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 may also conduct an independent on-site TSA during the verification test. The TSA findings will be communicated to testing staff at the time of the audit, and documented in a TSA report.

7.2.2 Performance Evaluation Audit

A performance evaluation (PE) audit will be conducted to assess the quality of the measurements made in this verification test. This audit addresses 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 performance evaluation audit. This audit will be performed once during the verification test, and must be performed by analyzing a standard or comparing to a reference that is independent of standards used during the testing. For most of the key measurements, this audit will 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 will involve sampling with a second O_2 analyzer at the same point in the duct, and comparing results. Similar comparisons will 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 will be checked with a calibrated set of weights. Table 7-1 summarizes the PE audits that will be done. These audits will be the responsibility of Battelle staff, and will be carried out with the cooperation of EPA and contractor staff.

Table 7-1. Summary of PE Audits on RKIS 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 will be carried once during the period of operation at the RKIS. Battelle will supply the equipment needed to make the independent PE measurements. If agreement outside the indicated tolerance is found, the test will be repeated. Further failure to achieve agreement will result in re-calibration of the independent measurement device, or use of a different measurement device.

For mercury, this PE requirement is difficult, because of the absence of convenient absolute gas-phase mercury standards or independent measurement devices. Consequently, this audit will consist of spiking one or more Ontario Hydro sampling trains with known amounts of mercury, and conducting sample analysis on the train without sampling of combustion gas. If the CEMs undergoing verification do not determine particulate Hg, then only the impingers of the OH train will be spiked. A NIST-traceable Hg standard solution will be used for that purpose. Agreement of Hg determined in sample analysis with that spiked into the sample train is expected to be within 10 percent. 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. Response to PE audit results outside the expected tolerance will be to consider possible causes for the disagreement, and if appropriate to note the implications of Ontario Hydro PE results on CEM verification results, in the verification reports. If determination of particulate Hg is performed by one or more of the CEMs undergoing verification, then a Hg standard will also be used to spike the particle filter in the OH train. Battelle's Quality Manager will assess PE audit results.

7.2.3 Data Quality Audit

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

7.2.4 Assessment Reports

Each assessment and audit will be documented in accordance with Section 2.9.7 of the QMP for the AMS pilot.[1] Assessment reports will 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 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 Quality Manager is authorized to stop work. Once the assessment report has been prepared, the Verification Testing Leader will ensure that a response is provided for each adverse finding or potential problem, and will implement any necessary followup corrective action. The Quality Manager will ensure that follow-up corrective action has been taken.

8.0 DATA ANALYSIS AND REPORTING

8.1 Data Acquisition

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

Data acquisition for the commercial CEMs undergoing verification will 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 will 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 Ontario Hydro sampling run, may also be provided, if available. If not provided, averaging will 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 will be recorded in laboratory record books maintained by Battelle, EPA, and contractor staff involved in the testing. These records will be 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, will be maintained. Separate files (including manual records, printouts, and/or electronic data files) will be kept for each CEM. At no time during verification testing will Battelle staff engage in any comparison or discussion of different CEMs.

Table 8-1 summarizes the types of data to be recorded; how, 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 is to be turned over to Battelle staff immediately upon completion of each test day. Identical file formats will be 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 will be overseen by the Verification Testing Leader and Quality Manager.

8.2 Data Review

Records generated in the verification test will 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 will be performed by a Battelle technical staff member involved in the verification test, but not the staff member that originally generated the record. EPA/contractor and/or vendor staff will be consulted as needed to clarify any issues about the data records. The review will be documented by the person performing the review by adding his/her initials and date to a hard copy of the record being reviewed. This hard copy will 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 5.0 will be conducted separately for each commercial Hg CEM. Separate verification reports will then be prepared, each addressing the CEM provided by one commercial vendor. The verification report will present the test data, as well as the results of the statistical evaluation of those data.

Table 8-1. 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/Contractor/ 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	Contractor/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	Contractor/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.

The verification report will briefly describe the ETV program and the AMS Center, and will describe the procedures used in verification testing. These sections will be common to each verification report resulting from this verification test. The results of the verification test will then be stated quantitatively, without comparison to any other CEM tested, or comment on the acceptability of the CEM's performance. The preparation of draft verification reports, the review of reports by vendors and others, the revision of the reports, final approval, and the distribution of the reports, will 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.

9.0 HEALTH AND SAFETY

The verification test described in this test/QA plan will be performed at the RKIS facility at EPA in Research Triangle Park, North Carolina. All participants in this verification test (i.e., Battelle, EPA, contractor, and vendor staff) will adhere to the health and safety requirements of the facility. Those requirements include completion of a 24-hour HAZWOPR training course before participation in any activities at the facility. Vendor staff will only be operating their Hg CEMs during the verification test. They are not responsible for, nor permitted to, operate the combustion source, or perform any other verification activities identified in this test/QA plan. 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 will be given a site-specific safety briefing prior to the installation and operation of the CEMs. This briefing will include a description of emergency operating procedures (i.e., in case of fire, tornado, laboratory accident) and identification and 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 mercury CEMs 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 will 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.

10.0 REFERENCES

1. Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Pilot, U.S. EPA Environmental Technology Verification Program, prepared by Battelle, Columbus, Ohio, September 1998.

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 (ICR) 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, Battelle, Columbus, Ohio, November 1998.