

A Comprehensive Evaluation of Flue Gas Mercury Speciation Methods

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Introduction

The 1990 Clean Air Act Amendments (CAAAAs) require the U.S. Environmental Protection Agency (EPA) to determine whether the presence of mercury and 188 other trace substances, referred to as air toxics or hazardous air pollutants (HAPs), in the stack emissions from fossil fuel-fired electric utility power plants poses an unacceptable public health risk (1). The EPA's conclusions and recommendations will be presented in two reports: "Utility Air Toxics Report to Congress" and "Mercury Study Report to Congress." The first congressional report will address the risk to public health, while the second report is to address both the human health and environmental effects of anthropogenic mercury emissions. The formal release of these reports, originally scheduled for 1993–1994, is being delayed pending additional review and more data (2). The National Institute of Environmental Health Sciences is also required by the CAAAs to investigate mercury and determine a safe threshold level of exposure.

The EPA, U.S. Department of Energy (DOE), and the Electric Power Research Institute (EPRI) have acknowledged that assessing the risk posed by power plant mercury emissions is very

complicated (3–5). Mercury is emitted in such small amounts that accurately measuring emission rates has been extremely difficult. In addition, researchers discovered that mercury is emitted in various physical and chemical forms, each possessing distinct properties that affect sampling and analysis methods.

Reliable mercury emission and ambient measurement methods are required to achieve the CAAA goal of assessing the potential human health risks from exposure to mercury. Specifically, accurate measurements of mercury emissions from fossil fuel-fired (fueled by coal, oil, or natural gas) power stations and ambient mercury concentrations in the environment are required for a variety of reasons, including the following:

- To estimate the anthropogenic flux of mercury to the environment on a local, regional, and global scale
- To identify atmospheric transport and transformation processes
- To accurately determine background and natural mercury concentrations
- To determine deposition and methylation mechanisms in ecosystems
- To assess human health risks
- To assess mercury bioaccumulation and the need to regulate the emissions from stationary sources
- To ensure compliance of sources with emission regulations, should they become necessary
- To determine partitioning among the various effluents of fossil fuel combustion systems
- To evaluate the removal efficiency of control technologies

In addition to measuring total mercury accurately, the identification and quantification of individual physicochemical forms (i.e., species) of mercury are imperative for addressing questions concerning mercury toxicity, bioaccumulation, emission control, and atmospheric fate and transport, because each has distinctive physical, chemical, and biological properties. Mercury emissions from anthropogenic sources occur in three main forms: solid particle-associated mercury; gaseous divalent mercury, Hg^{2+} ; and gaseous elemental mercury, Hg^0 . Estimates of the relative proportions of these species in fossil fuel-fired power plant emissions and in ambient air are scarce because of a lack of reliable sampling and analysis methods for the different mercury species. Currently, no validated method exists for determining mercury speciation in combustion flue gas or in the atmosphere.

EPRI and DOE are cosponsoring a research program at the Energy & Environmental Research Center (EERC) to evaluate mercury speciation analysis methods for electric utility power plants.

The EERC has implemented an extensive testing program using a bench-scale flue gas simulator and a pilot-scale combustion system to evaluate the performance characteristics (sensitivity, precision, bias, specificity, and interferences) for many of the mercury speciation methods.

Objectives

For the past 3 years, a substantial amount of work has been done at the EERC to evaluate sampling and analysis methods for determining mercury speciation in flue gas from fossil fuel combustion. To be utilized for coal combustion processes, mercury speciation measurement methods must be able to measure mercury at relatively low levels. Mercury concentrations in coal combustion flue gas can range from 1 to 30 $\mu\text{g}/\text{Nm}^3$; typical concentrations are from 5 to 12 $\mu\text{g}/\text{Nm}^3$. In addition, the methods must be sensitive enough to accurately measure within $\pm 0.5 \mu\text{g}/\text{Nm}^3$ with no interferences from other flue gas constituents. In testing these methods, the first objective was to determine whether they could reliably measure total mercury. In general, this is accomplished by using known standards or measuring versus a reference method. EPA Method 101A has been shown to be a validated reference method for total flue gas mercury and was used to make the comparisons.

Assuming a method can measure total mercury accurately, the next objective (the purpose of the project) was to determine whether a given method could speciate mercury in combustion flue gases. Unfortunately, there are no reference methods to which comparison can be made for mercury speciation. Therefore, tests were made with known mercury concentrations. Although known mercury concentrations can be added to the flue gas stream, there is no guarantee that the mercury will not convert to another form of mercury in the gas stream. Therefore, in evaluating mercury speciation methods, it was important to distinguish between gas-phase mercury reactions occurring in the flue gas and liquid-/solid-phase reactions occurring in the sampling trains.

Descriptions of Mercury Measurement Methods Tested

Sampling Train Methods. The most common approach for measuring mercury emissions from anthropogenic point sources, such as sites of fossil fuel combustion, is to extract a representative sample of the flue gas using a sampling train. Sampling trains generally consist of an isokinetic nozzle and a filter to collect a representative fly ash sample and a liquid or solid sorption system to collect a particulate-free gaseous sample. A variety of liquid and solid sorbents can be used to separate and preconcentrate gaseous mercury species. After sampling, the filter and sorption medium are prepared and analyzed for mercury in a laboratory. All impinger-based methods proposed for determining mercury speciation are configured similarly to the EPA Method 5 sampling train shown in Figure 1.

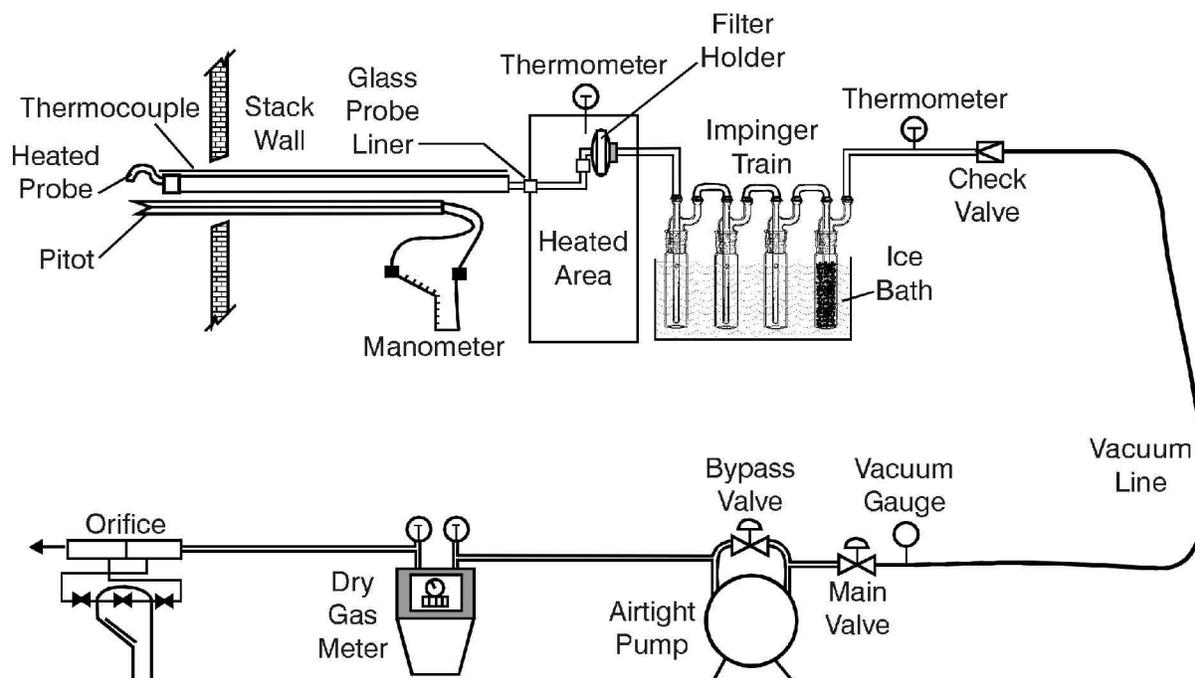


Figure 1. Schematic of the EPA Method 5 sampling train.

The EPA has developed and validated two methods, 101A and 29, for quantifying total mercury emissions from stationary sources such as fossil fuel-fired utility boilers. Method 101A was designed specifically for determining only the total emission of mercury. EPA Method 29, also known as the multiple metals stack emission measurement method, was developed for measuring the solid particulate and gaseous emissions of mercury and 16 other trace elements (antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, nickel, phosphorus, selenium, silver, thallium, and zinc).

Although the EPA Method 29 sampling train was not originally designed for mercury speciation analysis, various research groups, including the EERC, have reported tentative speciation results based on the method. Researchers surmised from the physical and chemical properties of mercury species that $\text{Hg}^{2+}(\text{g})$ and $\text{Hg}^0(\text{g})$ would be selectively absorbed in the separate acidified hydrogen peroxide ($\text{HNO}_3\text{-H}_2\text{O}_2$) and acidified permanganate ($\text{H}_2\text{SO}_4\text{-KMnO}_4$) solutions, respectively, used in the EPA Method 29 impinger train. Ongoing experimental investigations indicate, however, that the validity of these assumptions is incorrect. As a consequence, several groups have proposed modifications to the impinger solutions used in EPA Method 29. Modifications of EPA Method 29 that have been tested at the EERC include the Ontario Hydro, tris-buffer, and Research Triangle Institute (RTI) methods.

EPA Method 29. A schematic of the EPA Method 29 sampling train is presented in Figure 2. As shown in Figure 2, the EPA Method 29 sampling train consists of seven impingers. Following an optional moisture knockout impinger, gaseous mercury species are selectively collected in two pairs of impingers connected in series containing different absorption solutions. A portion of the

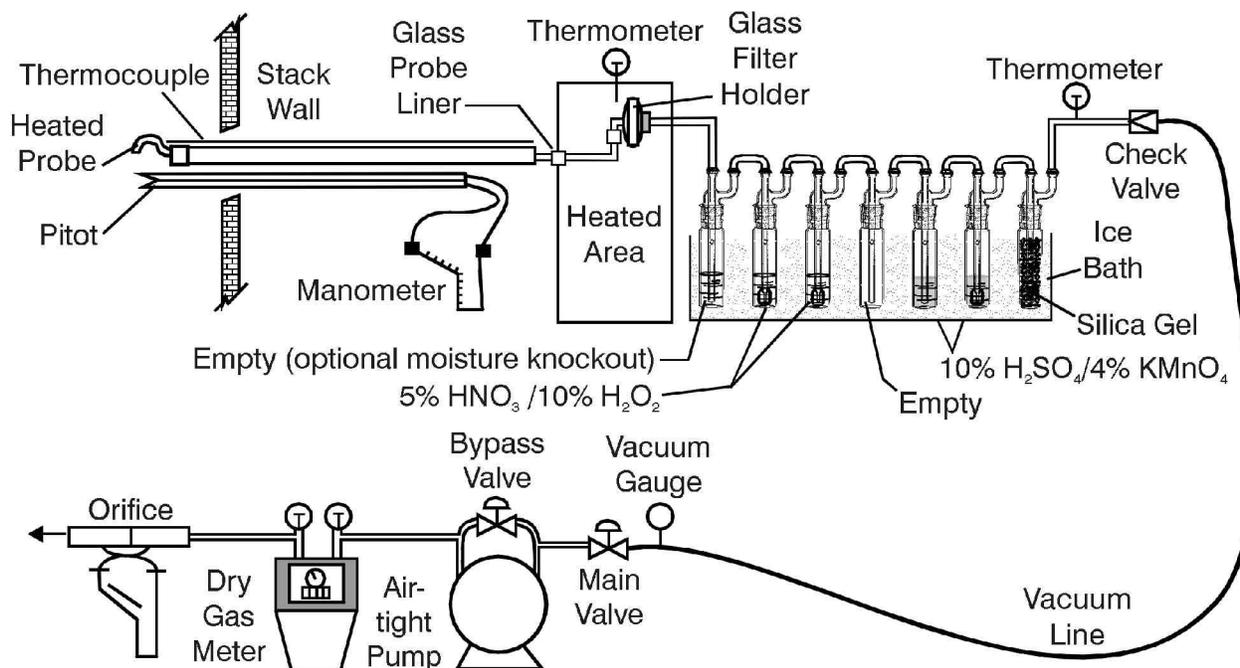


Figure 2. Schematic of the EPA Method 29 multimetal sampling train.

gaseous mercury is captured in the first pair of impingers containing aqueous solutions of 5% nitric acid (HNO_3) and 10% hydrogen peroxide (H_2O_2), while the remainder is captured in a second pair of impingers containing aqueous solutions of 4% potassium permanganate (KMnO_4) and 10% sulfuric acid (H_2SO_4). An empty impinger is located between the two sets of impingers to reduce the potential for blowback of KMnO_4 into the second HNO_3 - H_2O_2 impinger during leak checks. The last impinger in both sampling trains contains silica gel to prevent contamination and entrap moisture that may otherwise travel downstream and damage the dry-gas meter and pump.

Although EPA Method 29 is validated for determining total mercury emissions and some other trace elements from power plants, it has not been validated for determining mercury speciation. In fact, (as discussed later in this report) the data indicate that the two different impinger solutions employed are ineffective for reliably separating the Hg^{2+} and Hg^0 forms in a chemically complex flue gas.

Some of the practical limitations of the impinger-based methods originate from the problems and difficulties of using complex sample trains in the field that are composed of relatively large amounts of glassware and tubing. In addition, the glass impingers contain strongly oxidizing and acidic reagents requiring complex sample recovery and analysis procedures.

Ontario Hydro Method. This method was developed by Keith Curtis and other researchers at Ontario Hydro Technologies, Toronto, Ontario, Canada, in late 1994. Since testing with EPA Method 29 appeared to show that some of the Hg^0 was captured in the HNO_3 - H_2O_2 impingers, an attempt was made to more selectively capture the Hg^{2+} by substituting three aqueous 1N potassium chloride (KCl) impinger solutions for one of the HNO_3 - H_2O_2 solutions. A schematic of

the impinger train is shown in Figure 3. In the first tests using this concept, there were no acidified peroxide impingers in the sampling train. However, it was discovered that when the sulfur dioxide (SO_2) concentration in the flue gas was greater than approximately 750 ppm, the allowable sampling time was very short because the SO_2 reacted with the KMnO_4 and neutralized it. To avoid this problem, an impinger of acidified peroxide solution was used directly following the two KCl impingers. The purpose of the H_2O_2 was to absorb the SO_2 , thus protecting the acidified permanganate solutions. It is assumed that any mercury collected in the acidified peroxide solution was Hg^0 , since the KCl solutions would collect all of the Hg^{2+} .

Tris-Buffer Method. This method was developed by Radian International with the support of EPRI's Environmental Control Technology Center (ECTC). A tris(hydroxymethyl) aminomethane buffer solution (abbreviated tris) is substituted for the HNO_3 - H_2O_2 solutions in the first set of impingers of EPA Method 29, as shown in Figure 4. Myshkin and Konyaeva (6) demonstrated that tris forms trigonal complexes with Hg^{2+} in alkaline and neutral media. Testing by Radian International indicated that the addition of an ethylenediaminetetraacetic acid (EDTA) chelating agent to tris is required to effectively retain mercury chloride (HgCl_2). Evaluation results indicate that the tris-EDTA mixture is an effective SO_2 capturing solution. A negative aspect of this modification, however, is that sampling time must be reduced to about 45 min to a pH of 6 to be effective. In addition, recovery of mercury from the tris solution hour because the tris solution must be maintained at a is complex. During addition of HNO_3 and H_2O_2 to preserve the mercury in solution, carbon dioxide is evolved rapidly, so great care must be exercised to prevent loss of the mercury-containing tris solution.

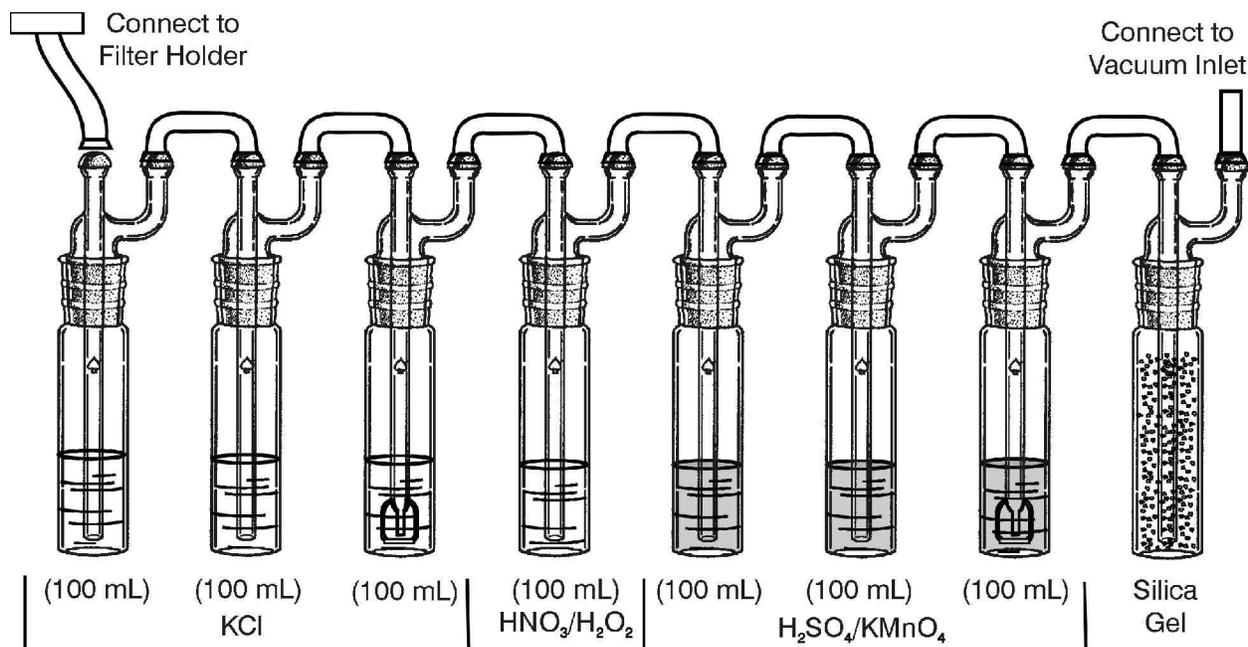


Figure 3. Schematic of the Ontario Hydro impinger train.

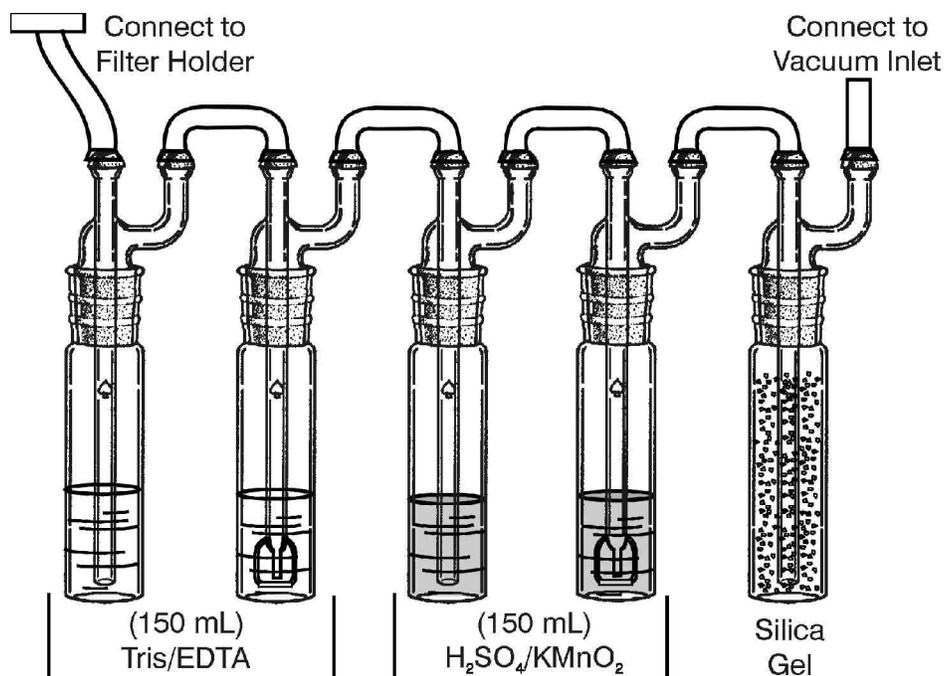


Figure 4. Schematic of the tris-buffer impinger train.

Research Triangle Institute Method. Researchers at RTI modified EPA Method 29 by replacing the first $\text{HNO}_3\text{-H}_2\text{O}_2$ impinger solution with deionized (DI) water, as shown in Figure 5. Initial evaluations of the RTI impinger train assembly are encouraging, although additional testing is required for a complete evaluation. The presence of high concentrations of SO_2 in a flue gas may interfere with the selective capture of Hg^{2+} by the water.

Mercury Speciation Adsorption Method (MESA). In addition to impinger-based sampling trains, gaseous mercury species, Hg^{2+} and Hg^0 , can be selectively captured on solid sampling medium through adsorption, amalgamation, diffusion, and ion exchange processes. Solid sorbents offer several advantages relative to liquid sorbents, including greater stability and easier handling and that the mercury collected can be analyzed directly using sensitive techniques such as atomic fluorescence. These advantages provide impetus for the development of solid sorption methods.

The MESA method was developed by researchers at Brooks Rand, Ltd., and Frontier Geosciences, Inc. The method was designed to measure of Hg^0 , Hg^{2+} , and monomethyl mercury (MMHg) compounds. A series of KCl-soda-lime and iodized activated carbon sorbents are used for sampling, and gas chromatographic separation, dual-gold amalgamation, and cold-vapor atomic fluorescence spectrometry (CVAFS) are used for analysis.

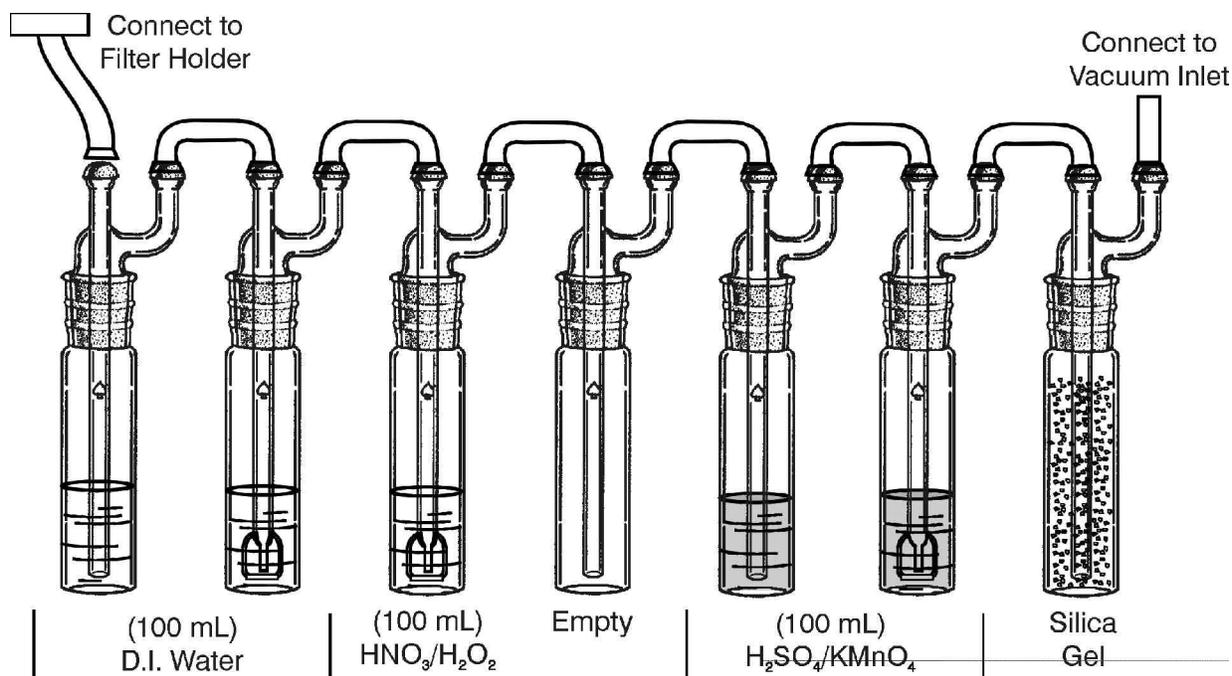


Figure 5. Schematic of the RTI impinger train.

The MESA sampling train, depicted in Figure 6, employs two pairs of heated solid sorbent traps in tandem. Two traps of each solid sorbent, a sample trap followed by a breakthrough trap, are used to optimize and evaluate collection efficiency. The flue gas is extracted nonisokinetically from a single point away from the flue duct walls through a small (0.32-cm) inlet orifice of a heated quartz tube. Particles entering the system are collected on either an inserted quartz wool plug or on the glass wool plug of the first trap. After extraction, the flue gas is drawn into the first pair of traps, containing KCl–soda-lime granules, and then through a pair of iodized activated carbon traps. Gaseous MMHg species and Hg^{2+} are adsorbed by the KCl–soda-lime trap, while Hg^0 is adsorbed by the iodized activated carbon trap. The sample train is maintained at $90^\circ \pm 2^\circ\text{C}$ to inhibit the condensation of water and Hg^{2+} breakthrough of the KCl–soda-lime traps.

The iodized activated carbon traps are digested individually in a mixture of HNO_3 and H_2SO_4 by refluxing. After the digest is diluted with doubly deionized water, mercury is determined by stannous chloride (SnCl_2) reduction, dual-gold amalgamation, and CVAFS.

In utilizing the MESA method, it is assumed that the mercury content of the particulate fraction is negligible; therefore, a single-point, nonisokinetic sample is acceptable. This assumption, however, does not always apply, and the nonquantitative collection of particulate is a major limitation of the current MESA method. Also, the capability of the method to accurately Hg^{2+} and Hg^0 in the presence of other flue gas constituents, especially NO_x in the presence of SO_2 , is suspect, as discussed below.

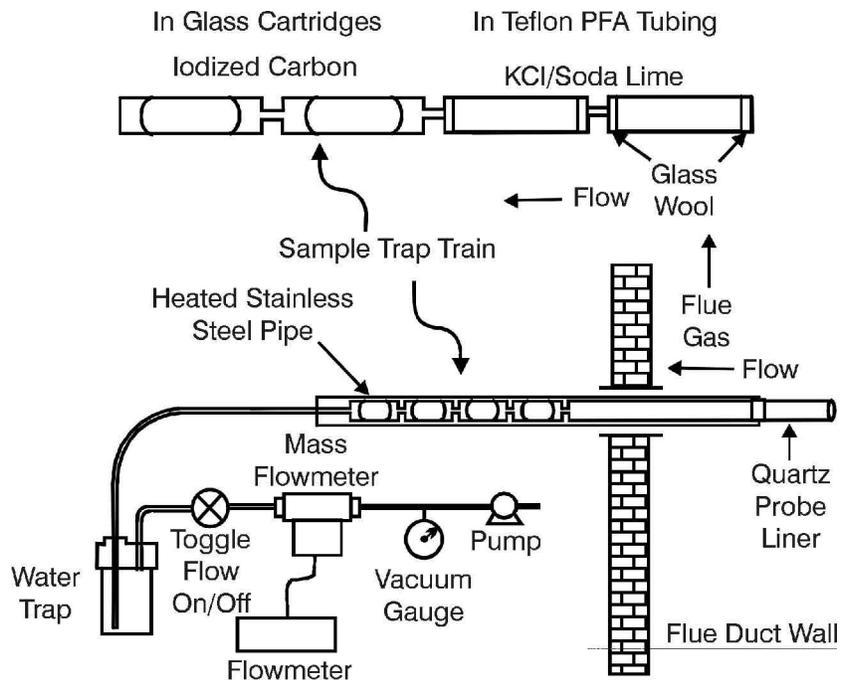


Figure 6. Schematic of the MESA sampling train.

Continuous Emission Monitors for Mercury. In addition to the sampling train methods described in the preceding section, automated on-line mercury analyzers are being developed based on the well-established techniques of cold-vapor atomic absorption spectrometry (CVAAS), CVAFS, and atomic emission spectroscopy (AES), as well as on the emerging technology of chemical microsensors. The analyzers can be used to directly measure Hg^0 in fossil fuel combustion flue gas on a continuous or semicontinuous basis. The analyzers can also be equipped with converters for reducing Hg^{2+} forms to Hg^0 so that total mercury can be determined and the Hg^{2+} concentration can be estimated by difference. Although on-line emission analyzers can be costly to purchase, install, and maintain, they offer several benefits, including the following:

- An analyzer can be used for feedback process control of mercury control systems, thus maximizing removal efficiency.
- A well-designed analyzer requires minimal operator input.
- An analyzer can provide information on the temporal variations in mercury emissions for a process that may be variable in its emission characteristics.
- An accurate analyzer could provide a timely regulatory compliance assessment, should it become necessary.

On-line mercury emission analyzers can be categorized as either extractive or in situ. Extractive analyzers are distant from the sampling location; therefore, a flue gas sample is removed,

transported, and conditioned before it actually enters the mercury analyzer. In situ mercury emission analyzers are mounted on the stack or duct and do not require sample transport or gas conditioning. All on-line analyzers utilize elaborate calibration systems. This report discusses three mercury CEMs that have been used in bench- and pilot-scale tests at the EERC. These are the Semtech Hg 2000, P.S. Analytical Sir Galahad, and the Perkin Elmer MERCEM.

Perkin Elmer MERCEM. The commercial Perkin Elmer mercury continuous emission monitor (MERCEM) determines total gaseous mercury. The MERCEM employs a sample probe containing two sintered metal filters to extract a particulate-free flue gas sample. A 185°C sample line is used to transport the sample gas to the conditioning and analysis units depicted in Figure 7. A SnCl₂ solution is injected into the sample line and transported concurrently with the sample gas to a reactor for converting Hg²⁺ to Hg⁰. After passing through a cooler to remove moisture, the dry sample gas enters a gold trap for amalgamation. The trap is heated to release Hg⁰ from the gold for analysis via CVAAS. After purging, the gold trap is cooled to ambient temperature for the next amalgamation–analysis cycle. In addition to preconcentrating Hg⁰, the amalgamation technique eliminates the possibility of interferences from other flue gas components. The MERCEM has been certified by TUEV Rheinland for determining compliance with the German legal limit of 50 µg/Nm³ for total mercury emissions from waste incinerators.

Semtech Hg 2000 (Sweden). The commercial Semtech Hg 2000 instrument (Semtech Metallurgy AB, Lund, Sweden) is essentially a portable Zeeman-modulated CVAAS that can continuously monitor Hg⁰. The analyzer is also equipped with an on-line reduction unit, illustrated in Figure 8, for continuously monitoring total mercury. In the reduction unit, a reducing solution, such as SnCl₂ or sodium borohydride (NaBH₄), is pumped to the sampling

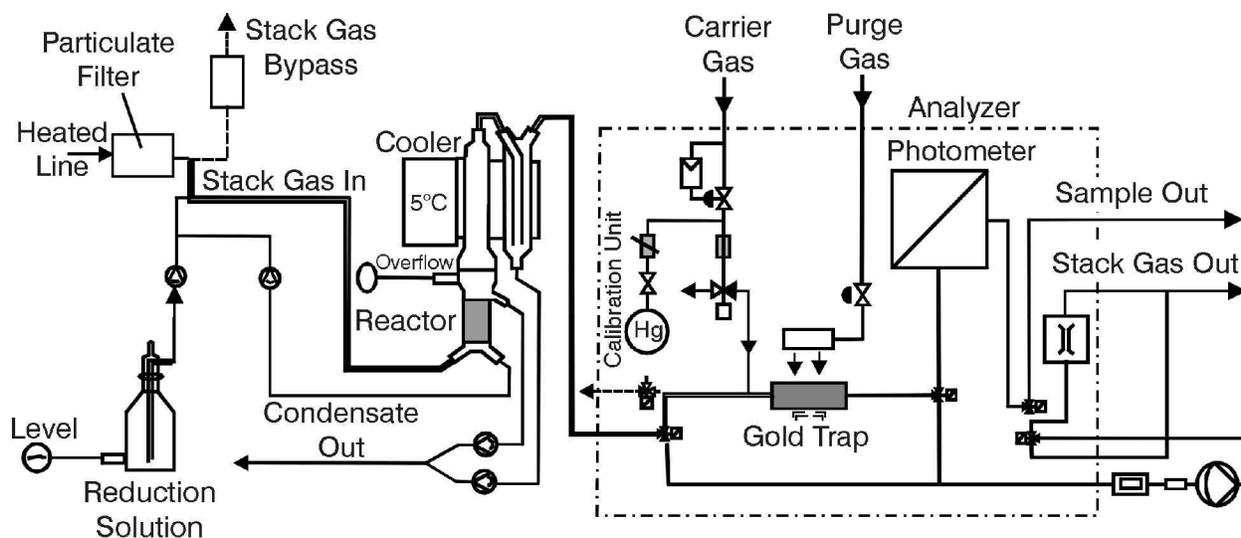


Figure 7. Schematic of the Perkin Elmer MERCEM.

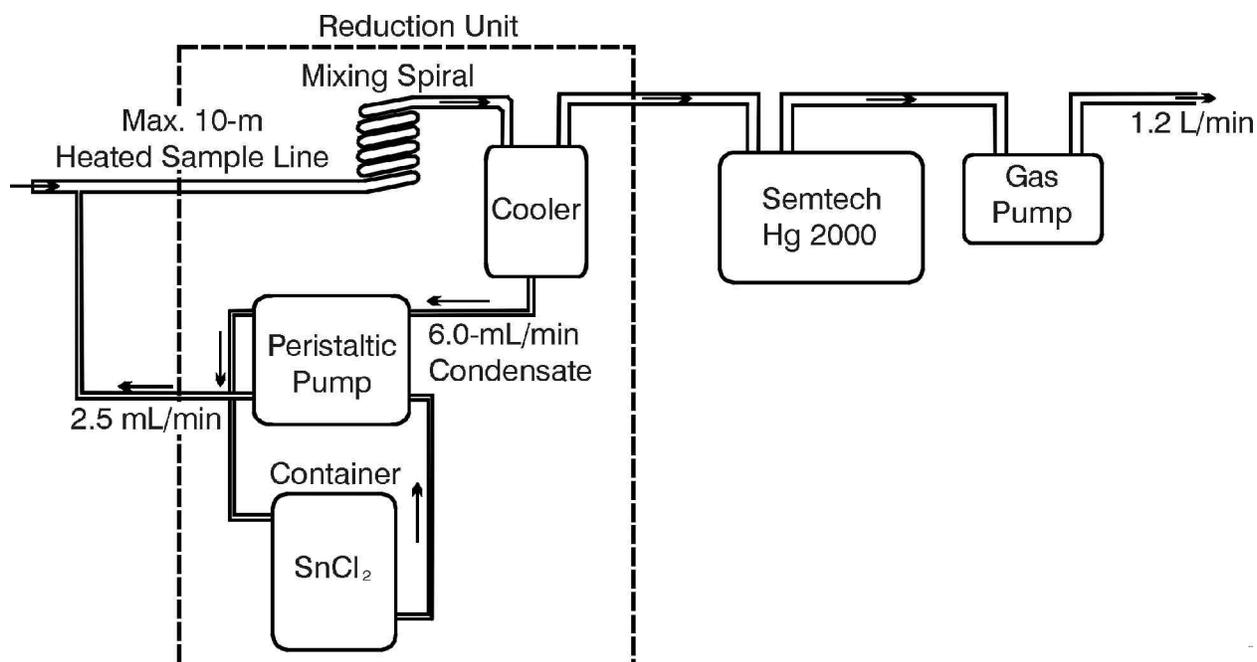


Figure 8. Schematic of the Semtech Hg 2000.

probe. The extracted gas sample and reducing solution are transported concurrently through a mixing spiral to maximize the gas–solution residence time and ensure the complete conversion of Hg^{2+} to Hg^0 . After converting to Hg^0 , the sample gas is transferred to a Peltier cooled gas–liquid separator. The conditioned dry gas is then analyzed using the Semtech Hg 2000 analyzer. The analyzer employs Zeeman effect background correction by applying a modulated magnetic field to a mercury lamp to minimize interferences from the presence of SO_2 , hydrocarbons, and particles in the flue gas sample. An operating range of $0.3 \mu\text{g}/\text{Nm}^3$ to $20 \text{mg}/\text{Nm}^3 \text{Hg}^0(\text{g})$ is specified by Semtech Metallurgy AB. The Semtech Hg 2000 has been certified by TUEV Rheinland for determining compliance with the German legal limit of $50 \mu\text{g}/\text{Nm}^3$ for total mercury emissions from waste incinerators.

P.S. Analytical Sir Galahad. The Sir Galahad analyzer was initially used to continuously monitor total mercury in the urban environment and natural gas, but it can also be used in a variety of gaseous media, including flue gas. The analyzer is based upon atomic fluorescence principles that provide an inherently more sensitive signal than the atomic absorption approach. The system employs gold-impregnated sand or a gold-impregnated silica support for preconcentrating mercury and separating it from potential interferences that degrade sensitivity.

To monitor for mercury in flue gas, a four-step process must occur. The first step involves pumping the flue gas (2 L) through a gold trap maintained at constant temperature. The gold trap is removed from the flue gas stream and placed into the analyzer. Before mercury is removed from the gold trap, a flushing step is initiated to remove any flue gas that may be present, as this would have a damping effect on the mercury fluorescence. When this is completed, the analysis

step begins. The heating coil is activated, which heats the gold trap to approximately 500°C. This desorbs the mercury on the trap, and the mercury is carried into the fluorescence detector. In preparation for the next loading stage, the gold trap is rapidly cooled by pumping argon over it. The total time for the entire process is about 5 min. The system can be operated manually or an automated system can be obtained from the company.

Calibration of the system is done using Hg^0 as the primary standard. It is contained in a closed vial held in a thermostatic bath. The temperature of the mercury is monitored, and the amount of mercury is calculated using vapor pressure calculations. Typically, the calibration of the unit has proven to be stable over a 24-hr period.

Results and Discussion

The EERC mercury speciation methods evaluation project that began June 1994 is expected to be completed by September of this year. Bench and pilot-scale tests have been completed evaluating four impinger-based methods (EPA Method 29, the Ontario Hydro method, the tris-buffer method, and the RTI method), a solid sorbent method (MESA), and three CEMs. These mercury measurement methods are described above.

Bench-Scale Results. A series of bench-scale tests to evaluate the mercury speciation ability of EPA Method 29 and other sampling techniques was performed at the EERC. In these tests, a wide range of flue gas constituents was added to the simulated flue gas stream along with either Hg^0 or HgCl_2 . Mercury permeation tubes, maintained at a constant temperature, were used to generate Hg^0 and HgCl_2 for these tests. A schematic of the EERC bench-scale system is presented in Figure 9. The gas concentrations used for these bench-scale tests are shown in Table 1. The test matrices used for the bench scale were either a replicated full or fraction factorial design used so that the minimum number of tests could be performed while still providing sufficient data for a statistical analysis of the effects of a number of variables.

EPA Method 29. The test matrices for the bench-scale tests to evaluate EPA Method 29 are shown in Tables 2 and 3 (these test matrices are referred to as Test Series I and II). A The statistical results from these two test series are shown in Table 4. **The + and - signs in the table indicate an increase or decrease in the percentage of elemental mercury collected in the acidified permanganate solution, respectively. An effect is significant if its absolute value is greater than the t-statistic found in the footnotes at the end of the table.**

As can be seen in Table 4, the addition of 1500 ppm of SO_2 to the flue gas results in about 10%–15% of the injected Hg^0 being captured in the acidified peroxide solution of EPA Method 29, thereby being reported as Hg^{2+} . The observed effect of SO_2 on mercury speciation by EPA Method 29 occurs in the acidified peroxide solution rather than as a gas-phase reaction. There is some evidence that certain trace metals, including mercury, may react with SO_2 to oxidize the metal (7). A possible mechanism that may explain how SO_2 in the aqueous phase may convert a portion of the Hg^0 vapor to the oxidized form is shown in the following two reactions:

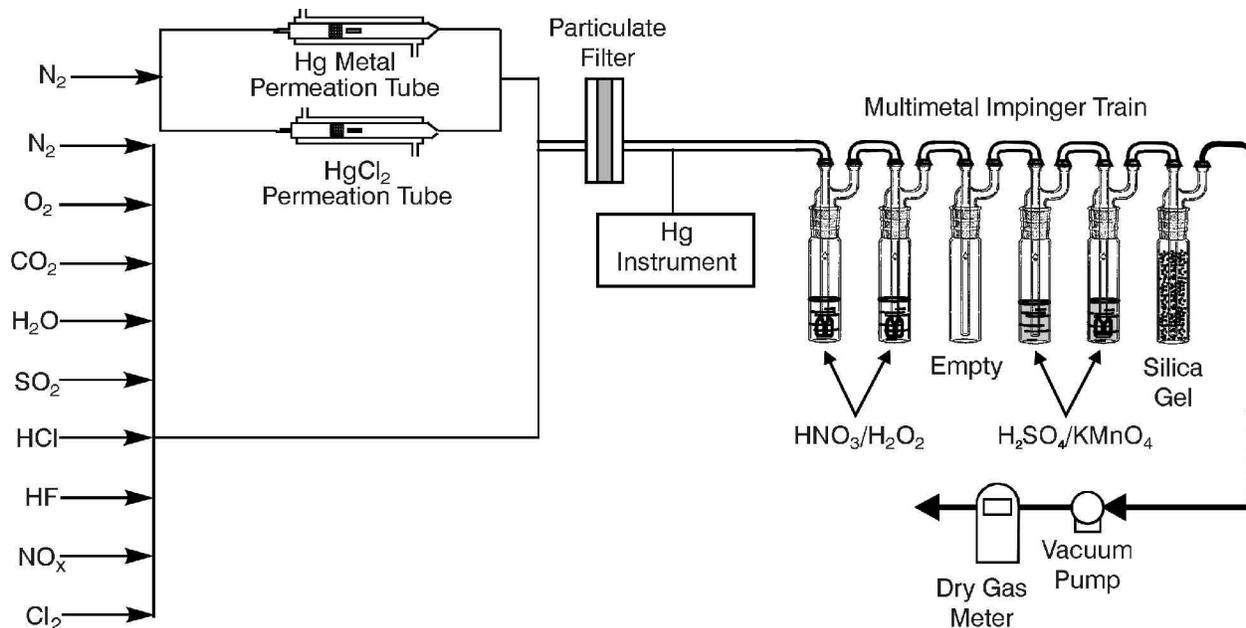


Figure 9. Schematic of the EERC bench-scale testing system.

TABLE 1

Gas Composition for the EERC Bench-Scale Tests (wet basis)	
	Concentration
Main Gases	
Oxygen	4%
Carbon Dioxide	15%
Water Vapor	10%
Nitrogen	Balance
Other Gases Used	
Sulfur Dioxide	1500 ppm
Hydrogen Chloride	50 ppm
Nitrogen Oxides	600 ppm
Elemental Mercury	20 $\mu\text{g}/\text{Nm}^3$
Mercury(II) Chloride	20 $\mu\text{g}/\text{Nm}^3$ (as Hg)
Hydrogen Fluoride	10 ppm
Chlorine	10 ppm

TABLE 2

Bench-Scale Test Matrix for EERC Test Series I^a

Test No.	Gas Composition	Hg ⁰ , $\mu\text{g}/\text{Nm}^3$	HgCl ₂ , $\mu\text{g}/\text{Nm}^3$	SO ₂ , ppm	HCl, ppm
1	Air	20	0	0	0
2	Simulated flue gas ^b	20	0	0	0
3	Simulated flue gas	20	0	1500	0
4	Simulated flue gas	20	0	0	50
5	Simulated flue gas	20	0	1500	50
6	Air	0	20	0	0
7	Simulated flue gas	0	20	0	0
8	Simulated flue gas	0	20	1500	0
9	Simulated flue gas	0	20	0	50
10	Simulated flue gas	0	20	1500	50

^a Gas temperature was 150°C.

^b Baseline simulated flue gas is composed of 4% oxygen, 15% CO₂, 10% H₂O, and a balance of N₂.

TABLE 3

Bench-Scale Test Matrix for EERC Test Series II^a

Test No.	Gas Composition	Fly Ash (Blacksville)	NO, ppm	Cl ₂ , ppm
1	Simulated flue gas ^b	N	0	0
2	Simulated flue gas	Y	0	0
3	Simulated flue gas	N	600	0
4	Simulated flue gas	Y	600	0
5	Simulated flue gas	N	0	10
6	Simulated flue gas	Y	0	10
7	Simulated flue gas	N	600	10
8	Simulated flue gas	Y	600	10

^a Gas and filter temperature was 120°C.

^b Baseline simulated flue gas is composed of 4% oxygen, 15% CO₂, 10% H₂O, 50 ppm HCl, 1500 ppm SO₂, 20 $\mu\text{g}/\text{Nm}^3$ Hg⁰, and a balance of N₂.

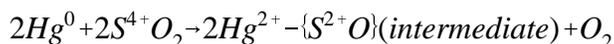
TABLE 4

Statistical Evaluation of EERC Bench-Scale Test Results for EPA Method 29				
Test Series No.	Variable	Main Effects	Two-Factor Interactions	Three-Factor Interactions
I ^b	SO ₂	-12.51 ± 0.95		
I	HCl	-1.36 ± 0.95		
I	SO ₂ × HCl		0.42 ± 0.95	
II ^c	Fly ash	-10.51 ± 0.56		
II	NO _x	2.77 ± 0.56		
II	Cl ₂	-44.21 ± 0.56		
II	Fly ash × NO _x		2.69 ± 0.56	
II	Fly ash × Cl ₂		5.91 ± 0.56	
II	NO _x × Cl ₂		1.39 ± 0.56	
II	Fly ash × NO _x × Cl ₂			-0.79 ± 0.56

^a Data in the table are based on the percentage of the measured mercury in the H₂SO₄-KMnO₄ solution while only Hg⁰ was injected.

^b Degrees of freedom for Test Series I is 10; two-tailed t-test is 95%; confidence is 2.228 (t-statistic is 2.228 × 0.95 = 2.117).

^c Degrees of freedom for Test Series II is 8; two-tailed t-test is 95%; confidence is 2.306 (t-statistic is 2.306 × 0.56 = 1.291).



From Table 4, it can be seen that HCl does not affect the speciation ability of EPA Method 29; however, chlorine gas (Cl₂) does. This is not entirely unexpected, because Cl₂ could react with the Hg⁰ to form HgCl₂ in a gas-phase reaction. However, the question that needs to be answered is whether Cl₂ exists in flue gas at the temperatures commonly found at particulate control devices and in stacks and, if so, at what concentration. Very little data are presented in the literature showing the speciation of HCl and Cl₂. However, in pilot-scale tests at the EERC (described later in this report), chlorine speciation measurements using EPA Method 26A were completed firing eastern bituminous coals. Results indicate that in flue gas containing more than 50 ppm of HCl, less than 1 ppm of Cl₂ was detected at the outlet of a particulate control device. However, results from the DOE Comprehensive Assessment of Toxic Emissions from Coal-Fired Power Plants show higher levels of Cl₂ (8). Therefore, questions have been raised about whether EPA Method 26A correctly speciates chlorine in flue gas with high SO₂ concentrations.

Finally, EERC bench-scale data indicate that fly ash appears to be important in determining mercury speciation in the flue gas stream. Fly ash collected from the pulse-jet baghouse hopper during pilot-scale tests firing a Blacksville coal was placed on a filter through which the simulated

flue gas was passed. All of the bench-scale test results, regardless of which sampling method was employed, showed that 10% to 12% of the injected Hg^0 was measured as Hg^{2+} when the simulated flue gas was passed through the fly ash bed. This is very strong evidence that at least some of the Hg^0 is converted to Hg^{2+} as it passes through the ash. Pilot-scale tests conducted by the EERC, Radian, and CONSOL tend to support this (9–11).

In Test Series I, no significant effects were observed from either SO_2 or HCl when HgCl_2 was injected. Therefore, subsequent bench-scale tests were conducted with the addition of Hg^0 only.

The Ontario Hydro Method. The Ontario Hydro method was evaluated at the EERC using a replicated fractional factorial design, which allowed five variables to be tested using a minimum number of tests. The test matrix is presented in Table 5 (Test Series III). The bench-scale test system and baseline flue gas concentrations were the same as previously described and shown in Table 1 and Figure 9. For the Ontario Hydro method, the effect of Blacksville fly ash was statistically significant, as indicated in Table 6. The data also show a strong negative effect of Cl_2 ; however, SO_2 had a positive effect. This may be due to the fact there was also a strong positive interaction between SO_2 and Cl_2 , which indicates that the presence of SO_2 may mitigate some of the effect of Cl_2 . However, the reasons for these results are unknown. In general the EERC bench-scale tests indicate that the Ontario Hydro method has the potential to accurately speciate mercury.

Tris-Buffer Method. Bench-scale evaluation of the tris-buffer method at the EERC was completed using the same replicated fractional factorial design that was used to evaluate the Ontario Hydro method. (The test matrix is shown in Table 5.) Table 7 details the statistical results of the bench-scale tests. As in the previous bench-scale tests at the EERC, the effects of the variables were determined by the percentage of the added Hg^0 that was measured by the tris-buffer method as Hg^0 . As shown in the table, the only flue gas constituents that show statistically significant effects were Cl_2 and Blacksville fly ash. As previously discussed, Cl_2 is generally not considered significant for coal-fired systems at temperatures commonly occurring in the stack. However, the effect of Blacksville fly ash on mercury speciation is significant, and it exerts its effect in the gas stream and not in the sampling solutions. This was shown in tests where a Semtech elemental mercury analyzer was placed just after a bed of Blacksville fly ash (the Semtech analyzer only measures Hg^0). The Semtech analyzer showed a decrease in Hg^0 ; however, an EPA Method 101A impinger train indicated a good mercury balance. Therefore, the Blacksville fly ash must be converting Hg^0 to Hg^{2+} , not absorbing the Hg^0 . From the bench- and pilot-scale results, it appears that some fly ashes play a significant role in determining the speciation of mercury emissions.

Mercury Speciation Adsorption Method (MESA). EERC bench-scale tests designed to evaluate the effects of various flue gas constituents on the MESA method were conducted using the same replicated full factorial test matrices and baseline flue gas as for the EPA Method 29 tests.

TABLE 5

Test Matrix for EERC Bench-Scale Test Series III: Fractional Factorial Design^{a,b}

Test No.	Fly Ash (Blacksville)	SO ₂ , ppm	HCl, ppm	NO/NO ₂ , ppm	Cl ₂ , ppm
1	N	0	0	0	10
2	Y	0	0	0	0
3	N	1500	0	0	0
4	Y	1500	0	0	10
5	N	0	50	0	0
6	Y	0	50	0	10
7	N	1500	50	0	10
8	Y	1500	50	0	0
9	N	0	0	600/30	0
10	Y	0	0	600/30	10
11	N	1500	0	600/30	10
12	Y	1500	0	600/30	0
13	N	0	50	600/30	10
14	Y	0	50	600/30	0
15	N	1500	50	600/30	0
16	Y	1500	50	600/30	10

^a Simulated flue gas composition: 4% oxygen, 15% carbon dioxide, 10% water vapor, 20°µg/Nm³ elemental mercury, and a balance of nitrogen.

^b Gas and filter temperature was 175°C.

The results from a statistical evaluation of the data from the first two test series are given in Table 8. As shown in the table, SO₂, HCl, and Cl₂ have little or no effect on the mercury speciation ability of the MESA method. However, there was a significant effect when NO_x was added to the simulated flue gas. Up to 75% of the elemental mercury was collected in the KCl–soda-lime trap and reported as Hg²⁺. Previous work at the EERC and at DOE Pittsburgh Energy Technology Center (PETC) has shown that sodium-based SO₂ sorbents in the presence of SO₂ and water can convert NO to NO₂ at 95°C, which is the operating temperature of the MESA sampling train (12, 13). Therefore, a possible explanation for the observed results is that the same effect is occurring in the potassium-based trap of the MESA method, with the NO₂ oxidizing Hg⁰ to Hg²⁺. The conversion of NO to NO₂ is highly temperature-dependent and is not observed below 65°C or above approximately 150°C.

TABLE 6

Statistical Evaluation of EERC Bench-Scale Test Results for the Ontario Hydro Method ^{a,b}		
Variable	Main Effect	Two-Factor Interaction
Fly Ash	-12.97 ± 1.35	
SO ₂	22.70 ± 1.35	
HCl	-0.99 ± 1.35	
NO/NO ₂	-6.32 ± 1.35	
Cl ₂	-31.49 ± 1.35	
Fly Ash × SO ₂		-7.16 ± 1.35
Fly Ash × HCl		-2.72 ± 1.35
Fly Ash × NO/NO ₂		-7.10 ± 1.35
Fly Ash × Cl ₂		-0.84 ± 1.35
SO ₂ × HCl		4.53 ± 1.35
SO ₂ × NO/NO ₂		-3.73 ± 1.35
SO ₂ × Cl ₂		23.94 ± 1.35
HCl × NO/NO ₂		-5.29 ± 1.35
HCl × Cl ₂		-2.93 ± 1.35
NO/NO ₂ × Cl ₂		5.76 ± 1.35

^a Data in the table are based on the percentage of the measured mercury in the acidified permanganate solution while only elemental mercury is injected.

^b Degrees of freedom for Test Series III is 19; two-tailed t-test is at 95%; confidence is 2.093 (t-statistic is $2.093 \times 1.35 = 2.826$).

Later tests were completed to confirm whether SO₂ must be present to observe the large effect due to NO_x. These tests showed that when only NO_x was present, 100% of the mercury was collected in the iodated carbon trap and reported as elemental mercury. However, when 1500 ppm SO₂ was added to the simulated flue gas, 64% of the mercury was captured in the KCl–soda-lime trap and reported as oxidized mercury. This confirmed previous results, which showed that NO_x in the presence of SO₂ significantly impacts the mercury speciation ability of the MESA method. In 1993, Frontier Geosciences collaborated with the University of Göteborg in Sweden to study mercury in combustion flue gas using a natural gas-fired experimental burner at the St. Jörgens facility (14). The original goal of the work was to investigate the effects of SO₂, HCl, O₂, and temperature on mercury speciation in flue gas. The data were later reevaluated to determine the ability of the MESA method to speciate mercury in the presence of flue gas components such as SO₂, HCl, O₂, and NO_x. The effect of varying excess O₂ and port temperature was not statistically significant. However, the data show that the amount of Hg²⁺ increases as the SO₂ concentration increases in the presence of NO_x even when only Hg⁰ is added to the gas stream. For SO₂ concentrations between 1000 and 2500 ppm, the measured Hg²⁺ ranged from 60% to 75%, which agrees with the EERC bench-scale results.

TABLE 7

Statistical Evaluation of EERC Bench-Scale Test Results for the Tris-Buffer Method^{a,b}

Variable	Main Effects	Two-Factor Interactions
SO ₂	2.51 ± 2.02	
HCl	-1.15 ± 2.02	
Fly Ash ^c	-8.82 ± 2.02	
NO/NO ₂	-3.57 ± 2.02	
Cl ₂	-10.50 ± 2.02	
Fly Ash × SO ₂		0.33 ± 2.02
Fly Ash × NO/NO ₂		-1.83 ± 2.02
Fly Ash × HCl		-0.55 ± 2.02
Fly Ash × Cl ₂		-4.47 ± 2.02
SO ₂ × HCl		2.10 ± 2.02
SO ₂ × NO/NO ₂		1.51 ± 2.02
SO ₂ × Cl ₂		3.10 ± 2.02
HCl × NO/NO ₂		-0.41 ± 2.02
NO/NO ₂ × Cl ₂		1.60 ± 2.02
HCl × Cl ₂		-0.13 ± 2.02

^a The data in the table are based on the percentage of the measured mercury in the acidified permanganate solution while only elemental mercury is injected.

^b Degrees of freedom for Test Series III is 19; two-tailed t-test is at 95%; confidence is 2.093 (t-statistic is $2.093 \times 2.02 = 4.228$).

^c All fly ash used in this test series was from the Blacksville baseline tests.

Bench-scale tests were also performed at Frontier Geosciences to try to reproduce the EERC results and to determine whether the observed conversion of Hg⁰ occurs on the KCl-soda-lime traps and whether the conversion is temperature-dependent. The results did not show any significant conversion of Hg⁰ to Hg²⁺. However, the test conditions including temperature, flue gas concentration, surface effects, and residence time were quite different from those tested at the EERC. The gas temperature never exceeded 120°C, and the maximum SO₂ concentration tested was 500 ppm. These results show that the MESA method may not overestimate the fraction of Hg²⁺ at low SO₂ levels (<500 ppm) and at lower flue gas temperatures. It is also interesting to note that the MESA method did not appear to be affected by the addition of Cl₂. All of the impinger-based methods showed a substantial impact of Cl₂ in the bench-scale tests. The reasons for this are not clear and may need further investigation.

Pilot-Scale Results. The EERC test program, sponsored by EPRI and DOE, was initially an attempt to validate EPA Method 29 as a mercury speciation method using the criteria outlined in EPA Method 301. Later pilot-scale tests were designed to compare the EPA Method 29 results to

TABLE 8

Statistical Evaluation of EERC Bench-Scale Test Results for the MESA Method ^a				
Test Series No.	Variable	Main Effects	Two-Factor Interactions	Three-Factor Interactions
I ^b	SO ₂	-2.48 ± 0.86		
I	HCl	0.58 ± 0.86		
I	SO ₂ × HCl		-0.28 ± 0.86	
II ^c	Fly ash	-10.29 ± 3.01		
II	NO _x	-73.84 ± 3.01		
II	Cl ₂	0.79 ± 3.01		
II	Fly ash × NO _x		-9.59 ± 3.01	
II	Fly ash × Cl ₂		6.53 ± 3.01	
II	NO _x × Cl ₂		1.09 ± 3.01	
II	Fly ash × NO _x × Cl ₂			-6.54 ± 3.01

^a Data in the table are based on the percentage of the measured mercury in the iodated carbon trap while only elemental mercury is injected.

^b Degrees of freedom for Test Series I is 8; two-tailed t-test is at 95%; confidence is 2.306 (t-statistic is $2.306 \times 0.86 = 1.98$).

^c Degrees of freedom for Test Series II is 8; two-tailed t-test is at 95%; confidence is 2.306 (t-statistic is $2.306 \times 3.01 = 6.94$).

other mercury-sampling methods. These tests were conducted using the 580,000-kJ/hr (550,000 Btu/hr) pulverized coal pilot-scale combustor located at the EERC. A schematic of the pilot-scale combustor is shown in Figure 10. The unit generates approximately 5.7 m³/min (200 acfm) of flue gas at 177°C (350°F) and has a pulse-jet baghouse operating at an air-to-cloth ratio of approximately 1.2 m/min (4 ft/min). Originally, the bags were woven fiberglass; however, later pilot-scale tests used expanded-membrane, all-Teflon® GORE-TEX® bags to provide for higher collection efficiency of the fly ash and ensure no interaction between the mercury and the bag material. The average particulate collection efficiency for the fabric filter using the GORE-TEX® bags was >99.995% for all tests conducted. Most of the pilot-scale tests were conducted firing a Blacksville bituminous coal; however, several tests were performed with two different Western subbituminous coals. Also tests are currently being conducted using an Ohio blend bituminous coal.

EPA Method 301 Testing Using EPA Method 29. The first 4 weeks of pilot-scale testing at the EERC were an attempt to validate EPA Method 29 as a mercury speciation method using the criteria established in EPA Method 301. For all of the tests, the Blacksville bituminous coal was fired in the combustor. The carbon carryover in the ash was between 3% and 5% for all tests, as measured by loss on ignition (LOI). The LOI may be important, since it appears that the amount of particulate-associated mercury may be a function of the amount of carbon in the ash.

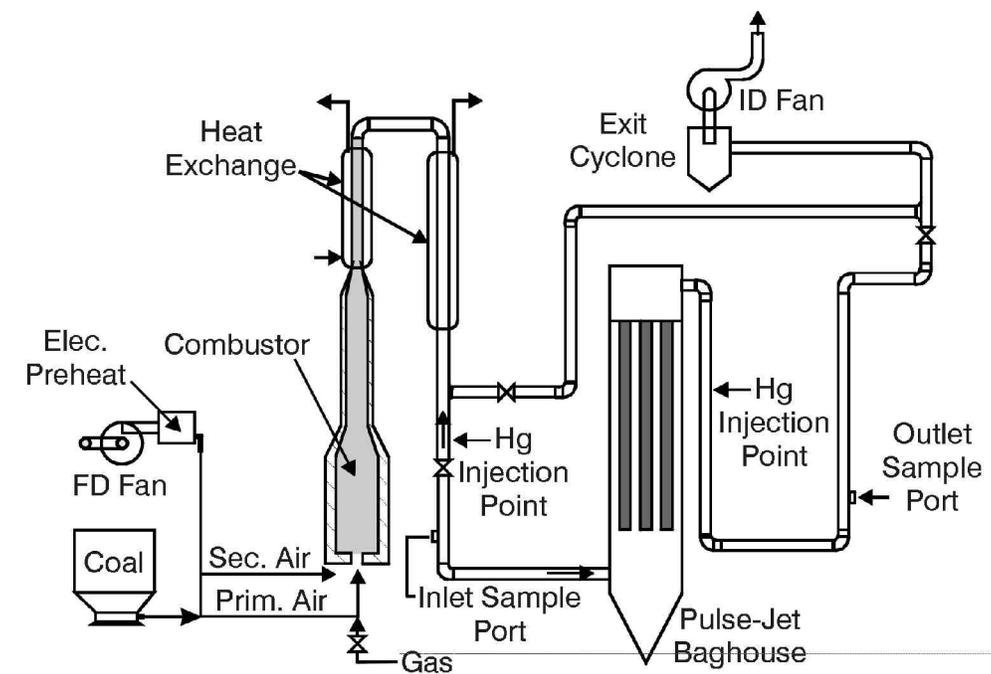


Figure 10. Schematic of the EERC particulate test combustor (PTC) and baghouse.

The first objective of these tests was to determine if EPA Method 29 measures total mercury correctly compared to the reference method, EPA Method 101A. The data in Figure 11 indicate reasonable agreement between the methods, and statistically, there is no difference between the methods at the 95% confidence level.

The data from the validation tests show that, statistically, EPA Method 29 is well within the EPA Method 301 criteria for both precision and bias, as shown in Table 9. The EPA Method 301 criteria are 0.7–1.3 for the bias correction factor and 50% relative standard deviation (RSD). Therefore, EPA Method 29 is a valid reference method for total mercury.

However, the data also indicate that when $8 \mu\text{g}/\text{Nm}^3$ of Hg^0 is continuously spiked into the flue gas stream, a substantial portion of the Hg^0 is measured as Hg^{2+} by EPA Method 29. Because the method was being evaluated for its ability to speciate mercury, this result made the data inconclusive. The question was whether the conversion was occurring in the flue gas stream or some of the added Hg^0 was being collected or converted to another mercury species in the acidified peroxide solution. This conversion of spiked Hg^0 is shown in Figure 12.

Approximately 85% of the Hg^0 spike was measured by EPA Method 29 as Hg^{2+} . Therefore it was necessary to conduct additional pilot tests to determine if EPA Method 29 was giving erroneous results or if conversion was occurring in the flue gas stream.

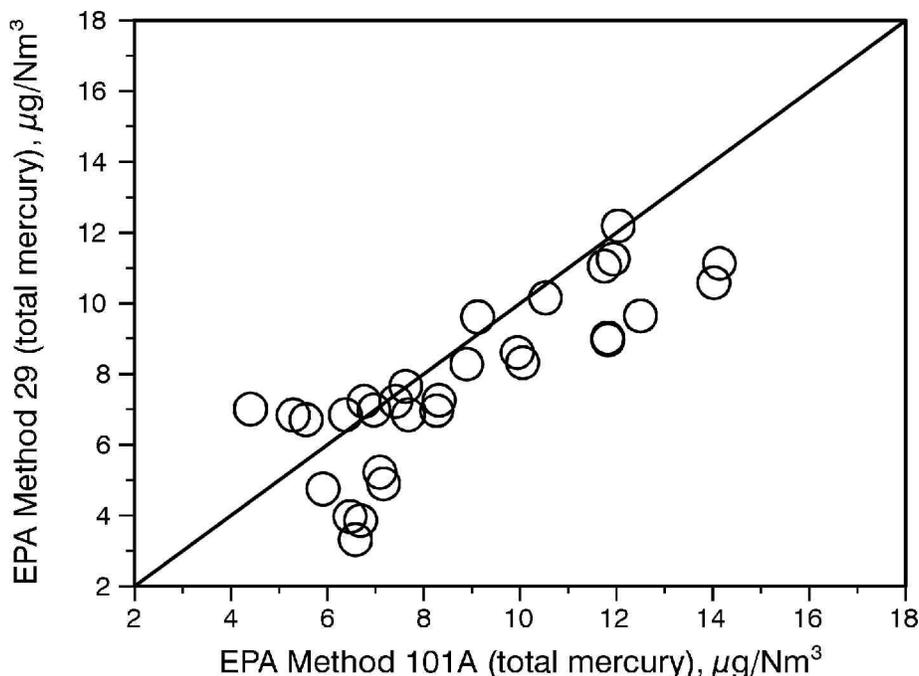


Figure 11. Comparison between EPA Method 29 and EPA Method 101A for total mercury.

TABLE 9

Statistical Results for EPA Method 301 Validation of EPA Method 29 with Hg⁰ Spiking

	HNO ₃ -H ₂ O ₂ Solution, µg/Nm ³	H ₂ SO ₄ -KMnO ₄ Solution, µg/Nm ³	Total Mercury, µg/Nm ³
Average, no analyte spike	10.17	4.00	14.17
Average, with analyte spike subtracted	9.19	3.78	12.97
Spike Recovery, %	89.2	93.1	—
Correction Factor	1.12	1.07	—
Relative Standard Deviation	9.4	13.9	4.8

Pilot-Scale Methods Comparison Tests. Additional pilot-scale tests were completed at the EERC for two related purposes. The first was to try to determine whether the observed conversion of Hg⁰ to Hg²⁺ as measured by EPA Method 29 was occurring in the gas stream or in the acidified peroxide solutions of the method. The second purpose was to provide data to help establish what flue gas components were affecting the ability of EPA Method 29 to speciate mercury. Tests were made comparing EPA Method 29 to four other proposed mercury speciation sampling methods, the Ontario Hydro, tris-buffer, RTI, and MESA methods.

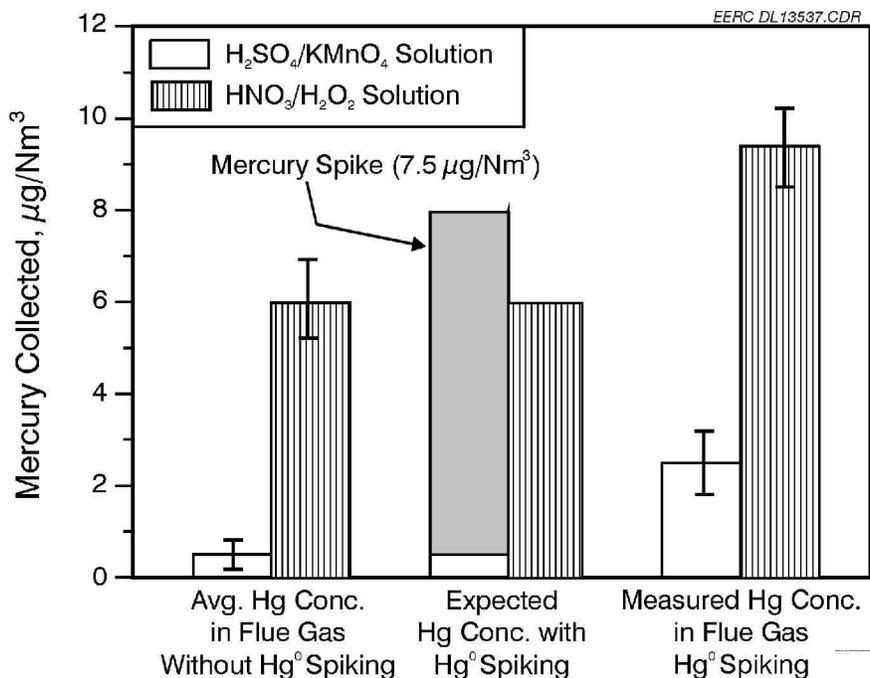


Figure 12. Observed conversion of spiked Hg⁰ to Hg²⁺ as measured by EPA Method 29 at the EERC (Blackville bituminous coal).

The first series of tests was completed firing natural gas in the PTC. EPA Method 29 was compared to the Ontario Hydro and MESA methods. The first natural gas test was a baseline, followed by tests where 1500 ppm SO₂ and 50 ppm of HCl were injected into the combustion zone. The results from these tests are shown in Figure 13. As can be seen in the figure, all of the methods tested, with the exception of the MESA method, showed insignificant conversion of Hg⁰ to Hg²⁺ when SO₂ and HCl were added. The pilot-scale results for the MESA method confirm the results of the bench-scale tests, that the MESA method substantially overestimates the Hg²⁺ in the presence of SO₂ and NO_x.

After the natural gas tests were completed, pilot-scale tests were done comparing the different mercury-sampling methods including the Ontario Hydro, MESA, and tris-buffer methods. The filter temperature was maintained at 177°C, as opposed to the earlier tests when the temperature was 120° ± 8°C. This temperature change allowed a direct comparison between the amount of mercury collected on the filter ash and the baghouse hopper ash. Figure 14 shows a comparison of EPA Method 29 to the MESA and Ontario Hydro methods when Hg⁰ is spiked into the flue gas upstream of the fabric filter. The data clearly show that all three methods measure a large portion of the Hg⁰ spike as Hg²⁺. It can also be noted that the MESA method showed the highest concentration of Hg²⁺, again supporting the bench-scale results.

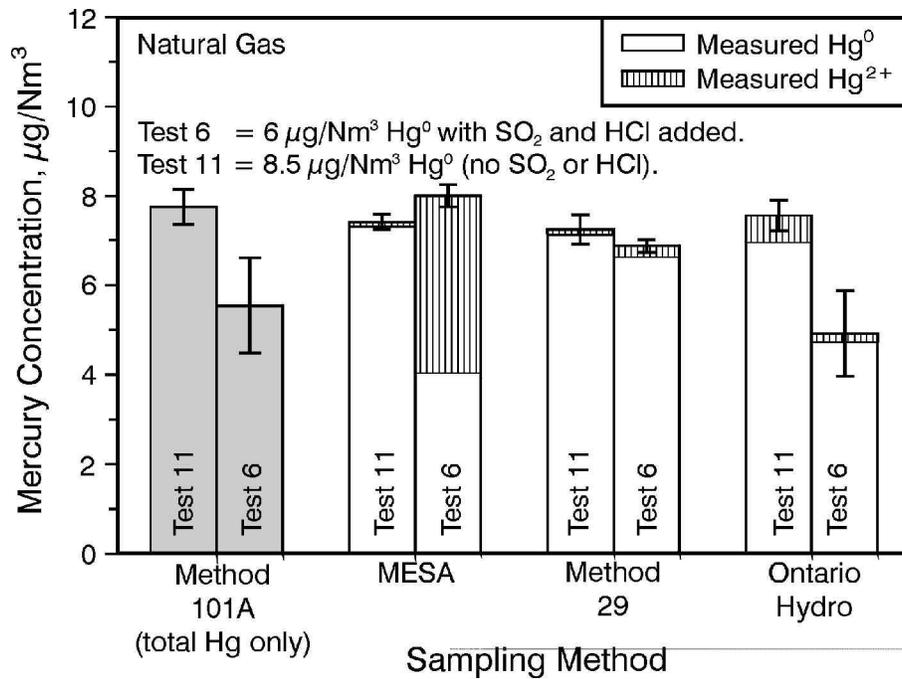


Figure 13. Comparison of mercury speciation sampling methods when natural gas was fired (error bars are for total mercury).

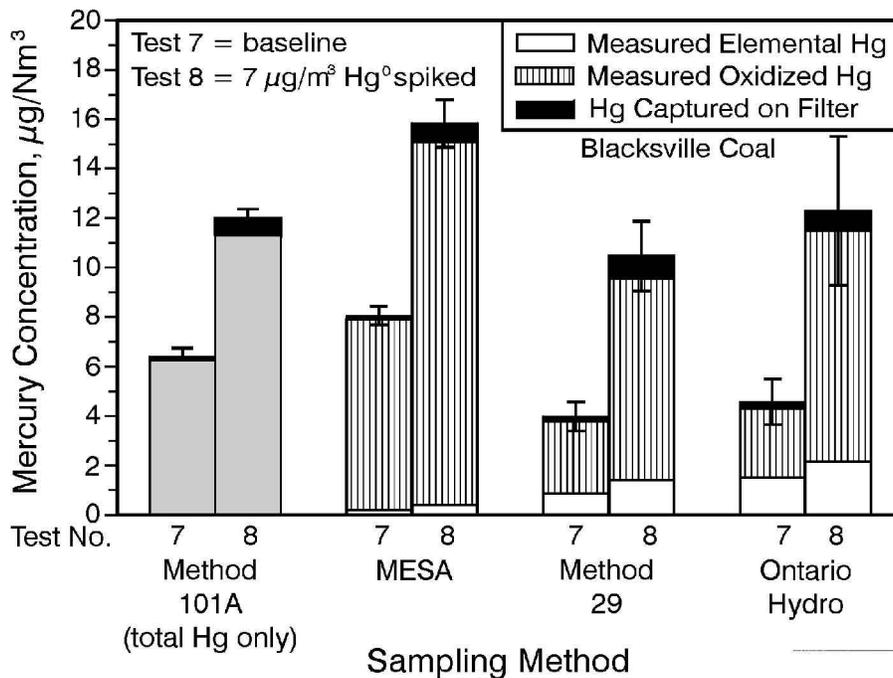


Figure 14. Mercury speciation comparisons when Hg^0 was spiked and sampling was completed at the baghouse inlet (error bars are for total mercury).

When identical tests were later conducted with the tris-buffer methods, the same results were apparent. Every mercury speciation method tested to date shows that when Hg^0 is spiked into the gas stream prior to the fabric filter while Blacksville coal is fired, substantial conversion of the Hg^0 spike to Hg^{2+} is measured. Although not conclusive, this presents strong evidence that the conversion occurs in the gas stream and not in the sampling trains.

When the same tests were conducted with Absaloka subbituminous coal, the observed conversion of Hg^0 to Hg^{2+} was not nearly as significant as shown in Figure 15. This was to be expected, since the baseline speciation data showed that the mercury in the flue gas was 85% Hg^0 . However, there does appear to be a small amount of conversion. It appears that for both the tests conducted firing Blacksville and Absaloka, conversion of an Hg^0 spike to Hg^{2+} is dictated by the $\text{Hg}^0/\text{Hg}^{2+}$ prior to the Hg^0 spike.

The results from the tests where Hg^0 was spiked into the flue gas stream upstream of the fabric filter appeared to show that the measured conversion of the spike was at least in part a gas stream reaction. However, it is still not conclusive whether the sampling methods are speciating correctly. Based on the effects of Blacksville fly ash observed in the bench-scale tests, it was decided to spike the Hg^0 downstream of the fabric filter. This was an attempt to eliminate the confounding effects of the fly ash. Figure 16 shows the results when sampling was done with the Ontario Hydro and tris-buffer methods. As can be seen, there is no conversion of the Hg^0 spike. Both methods under identical conditions (except spiking and sampling location) had shown substantial conversion when spiking was done at the fabric filter inlet. It has been conclusively shown that some fly ashes substantially affect mercury speciation. In addition, the pilot-scale

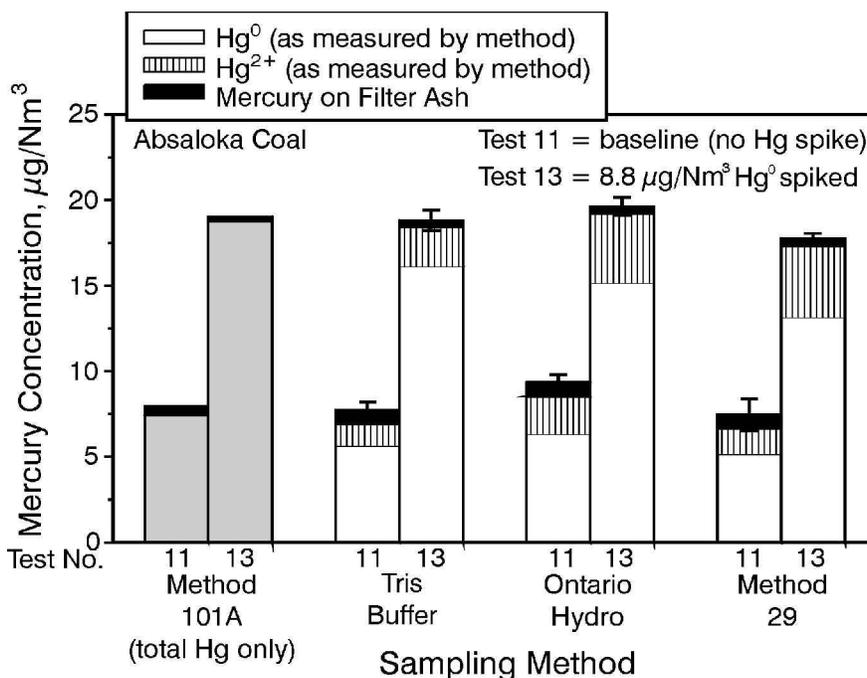


Figure 15. Method comparisons when Hg^0 sampling was performed at the baghouse inlet (error bars are for total mercury).

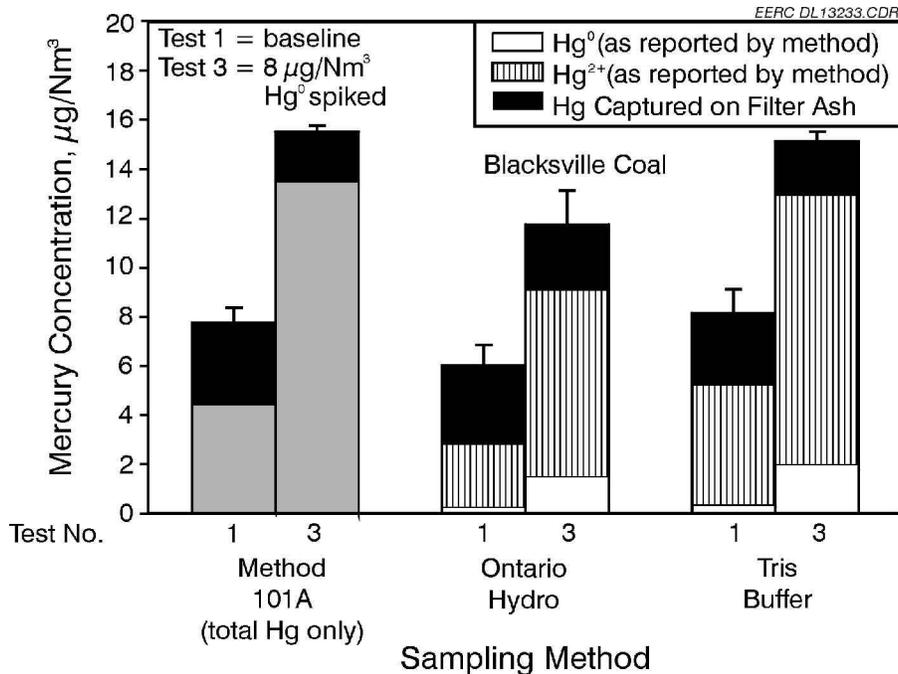
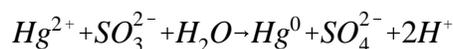


Figure 16. Comparison between the Ontario Hydro and tris-buffer methods when Hg⁰ was spiked and sampling was performed at the baghouse inlet (error bars are for total mercury).

data support the premise that the Ontario Hydro and tris-buffer methods both speciate mercury correctly.

Although the data using the Ontario Hydro method showed no conversion of the Hg⁰ spike, compared to EPA Method 101A and the tris-buffer method, the total mercury levels were somewhat low. The Hg⁰ concentrations were the same; however, the amount of mercury captured in the KCl solutions was lower than expected based on the other two methods and the known mercury balance. It appeared that mercury was being lost from the KCl solutions during sample preparation and analysis. It is possible that SO₂ accumulates in the KCl solution, which decreases the pH of the solution, resulting in Hg²⁺ being reduced according to the following chemical reaction:



If this were to occur, the mercury could easily be liberated during the sample preparation steps. To eliminate this possibility, KMnO₄ solution was added to the KCl solutions during sample recovery. The KMnO₄ neutralizes the SO₂ and preserves the mercury in solution. In later tests with two subbituminous coals, the Ontario Hydro results were more consistent with EPA Method 101A and the tris-buffer method for total mercury.

Once it was discovered that the tris-buffer and Ontario Hydro methods appear to speciate correctly at the fabric filter outlet, sampling was completed comparing EPA Method 29 to the tris-buffer method when Hg⁰ was spiked at the outlet while Blacksville coal was fired. The results are shown in Figure 17. As can be seen, approximately 35% of the spiked Hg⁰ was

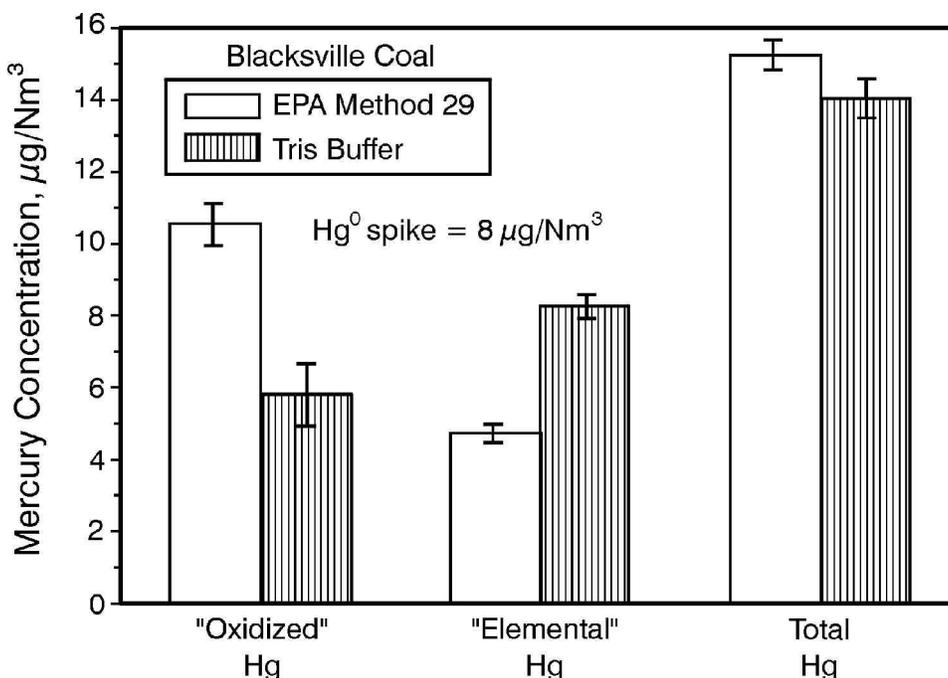


Figure 17. Mercury speciation comparison between EPA Method 29 and the tris-buffer method when spiking and sampling were performed at the baghouse outlet (Blacksville bituminous coal).

measured as Hg^{2+} using EPA Method 29. The tris-buffer method again measured the entire spike as Hg^0 .

Full-scale tests at an eastern U.S. utility (as part of Phase II of the DOE Comprehensive Assessment of Toxic Emissions from Coal-Fired Power Plants) were completed comparing EPA Method 29 to the Ontario Hydro Method (15). This power station is equipped with venturi scrubbers and cold-side ESPs for SO_2 and particulate removal. Mercury samples were taken both before and after the scrubbers. The SO_2 concentration was approximately 1400 ppm at the scrubber inlet and 200 ppm at the outlet. A comparison of the mercury speciation results for EPA Method 29 and the Ontario Hydro method at the inlet to the scrubber showed that EPA Method 29 overestimated the Hg^{2+} compared to the Ontario Hydro method. EPA Method 29 measured an increase in Hg^0 at the outlet of the scrubber compared to the inlet ($2.6 \mu\text{g}/\text{Nm}^3 \text{Hg}^0$ at the inlet compared to $4.4 \mu\text{g}/\text{Nm}^3 \text{Hg}^0$ at the outlet of the scrubber). This increase in Hg^0 at the outlet of the flue gas desulfurization (FGD) system almost the same percentage that EPA Method 29 overestimated the Hg^{2+} compared to the Ontario Hydro method at the inlet of the FGD system. These data, along with the pilot-plant data generated by the EERC and Radian International, are a strong indication that EPA Method 29 overpredicts the oxidized species of mercury by collecting some of the Hg^0 is in the $\text{HNO}_3\text{-H}_2\text{O}_2$ impingers.

Some limited pilot-scale tests were also completed using the RTI method. As discussed earlier, this method is a modification of EPA Method 29 where the first $\text{HNO}_3\text{-H}_2\text{O}_2$ impinger is replaced by two DI water impingers. The method is based on the principle that Hg^{2+} compounds are water-soluble, while Hg^0 is virtually insoluble.

Early in the mercury methods evaluation project at the EERC, discussions with Radian International were held to determine what mercury speciation methods were most promising and should be tested. Radian indicated that using water in place of the $\text{HNO}_3\text{-H}_2\text{O}_2$ solution in EPA Method 29 to absorb the Hg^{2+} would not work well. The problem was that SO_2 in the gas stream could result in the reduction of the captured Hg^{2+} to Hg^0 , with subsequent loss of mercury. When the EPA Office of Solid Waste decided to validate the RTI method at a cement kiln in South Carolina, it was also decided to conduct the limited pilot-scale tests at the EERC. The RTI method was compared to EPA Method 29, the tris-buffer method, and the Ontario Hydro method. A Blacksville bituminous coal, which generated about 1400 ppm of SO_2 in the flue gas, and a low-sulfur Powder River Basin subbituminous (Belle Ayr) coal, which generated only about 270 ppm of SO_2 , were used for these tests.

A 2-day Blacksville test was conducted comparing the RTI method to the tris-buffer method and EPA Method 29. Hg^0 was spiked, and the flue gas was sampled at the outlet of the baghouse. A comparison of the data for the three methods is shown in Figure 18. The inlet data from all Blacksville tests at the EERC indicate an average baseline Hg^0 concentration of $0.8 \mu\text{g}/\text{Nm}^3$. With an added Hg^0 spike of $7.5 \mu\text{g}/\text{Nm}^3$, the total Hg^0 concentration was $8.3 \mu\text{g}/\text{Nm}^3$ for a 100% Hg^0 balance. The tris-buffer method gave an elemental mercury balance of 99.4% compared to 89.5% for the RTI method and only 56.9% for EPA Method 29. The significance of the difference between the tris-buffer data and the RTI data needs further evaluation.

Additional pilot-scale tests were conducted firing a low-sulfur Belle Ayr coal comparing the RTI method to the tris-buffer and Ontario Hydro methods at the baghouse outlet. The results in Figure 19 show no statistical difference (based on the error bars) among these three methods. Additional tests are currently being conducted with the RTI method.

Pilot-Scale Results for Mercury CEMs. The Perkin Elmer MERCEM, the P.S. Analytical Sir Galahad, and the Semtech on-line mercury analyzers were evaluated during pilot-scale testing at the EERC. All of these instruments were described earlier in this paper. The Perkin Elmer is currently being used at five incineration facilities in Europe. The P.S. Analytical instrument has been used almost exclusively for measuring mercury in ambient air and in natural gas lines. This instrument has the capability of measuring very low levels of mercury in gas streams. The Semtech mercury analyzer was originally designed to measure only Hg^0 . A conversion cell has been added for measuring total mercury. When a bypass valve is used, Hg^0 can be measured, giving mercury speciation by difference. In bench-scale studies at the EERC and pilot-scale studies at the University of Göteborg, Sweden, the Semtech mercury analyzer worked quite well to measure Hg^0 (8).

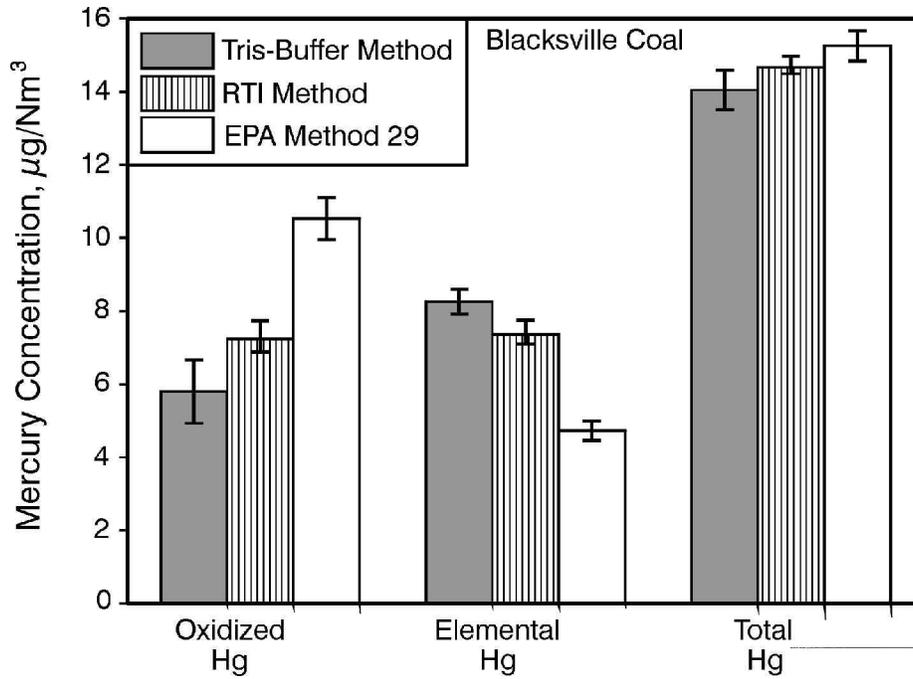


Figure 18. Mercury speciation comparisons when Hg⁰ was spiked and sampling was performed at the baghouse (error bars are for total mercury).

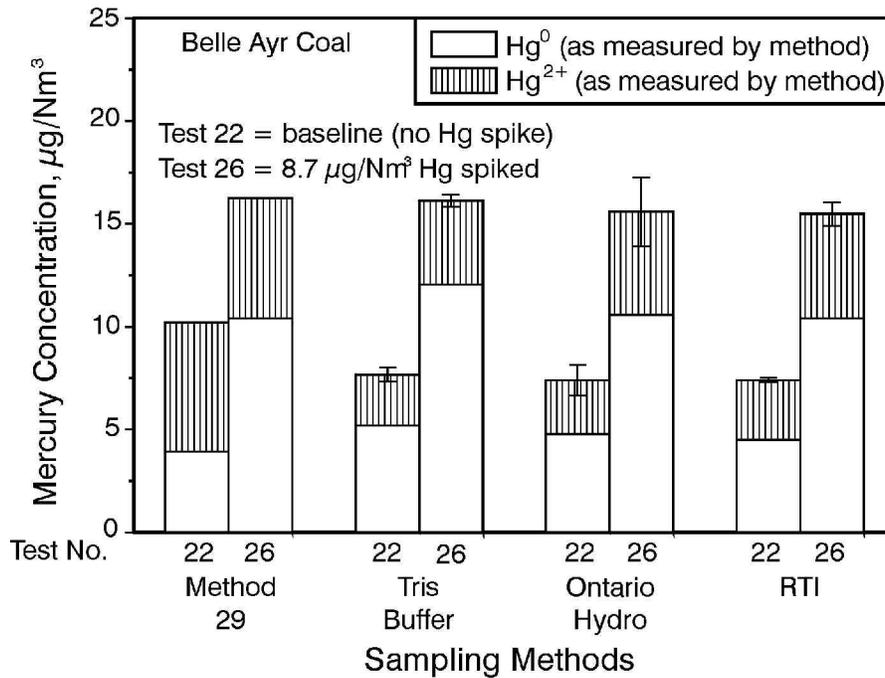


Figure 19. Mercury speciation comparisons when Hg⁰ was spiked and sampling was performed at the baghouse outlet (error bars are for total mercury).

All the analyzers were used to measure the baseline flue gas mercury concentration at the outlet of the combustor and also to determine the mercury concentration downstream of the flue gas mercury spike at the inlet or outlet of the pulse-jet baghouse. The only instrument data that could be compared to the impinger-based methods on a consistent basis were the data collected using the Perkin Elmer and P.S. Analytical instruments. The Semtech mercury analyzer, with the conversion cell, gave very low total mercury values compared to the wet chemistry results and the other mercury analyzers. It appeared that the conversion cell was not converting all of the mercury to elemental mercury so that the ultraviolet (UV) analyzer could detect it. This has now been corrected and has been used successfully in the EERC bench-scale tests evaluating mercury sorbents. The Semtech is again being evaluated in the currently on-going pilot-scale tests at the EERC. The results from these tests were not yet available for this report.

The Perkin Elmer, although a very large instrument, was almost maintenance-free during the 3 weeks of the test program at the EERC. Other than changing the particulate filter periodically, there were no maintenance activities with the instrument.

P.S. Analytical's Sir Galahad was used in the manual mode. In its current configuration, it requires a full-time technician. A gold trap must be inserted into the gas stream, and after the desired gas volume has been sampled, the trap must be removed and inserted manually into the instrument. The mercury is then desorbed, measured, and recorded on a computer. Therefore, the approximate time between samples was 10–15 min. P.S. Analytical has developed a front-end sampling system to fully automate sample collection and analysis. This should improve the overall performance achieved.

A comparison was made between the data generated using the Perkin Elmer and P.S. Analytical instruments to the different impinger-based mercury measurement methods. The total measured vapor-phase mercury concentration using the analyzers is plotted with the impinger-based results in Figures 20 through 23. For the purposes of this paper, the baghouse outlet instrument data are used because a more direct comparison can be made to the impinger-based data since the particulate mercury is very low. (Note: For the Ontario Hydro method, total mercury was low because KMnO_4 had not been added to stabilize the mercury collected in the KCl solutions). The filter for the Perkin Elmer CEM was maintained at $185^\circ\text{--}190^\circ\text{C}$ according to the manufacturer's specifications. However, the sample filters for the impinger-based trains were maintained at 177°C , the temperature of the flue gas at the sampling location. Since the amount of mercury captured on the sampling filter ash is highly dependent on temperature, more variability in the baghouse inlet data was noted. Figures 20 and 21 show a comparison of the measured total vapor-phase mercury from the mercury analyzers and impinger-based method with Hg^0 spiking, and Figures 22 and 23 show data from tests with HgCl_2 spiking. As shown, these analyzers gave reasonable results compared to the impinger-based methods. In most cases, the total vapor-phase mercury measured by the analyzers was within 20%–25% of the results from the impinger-based methods.

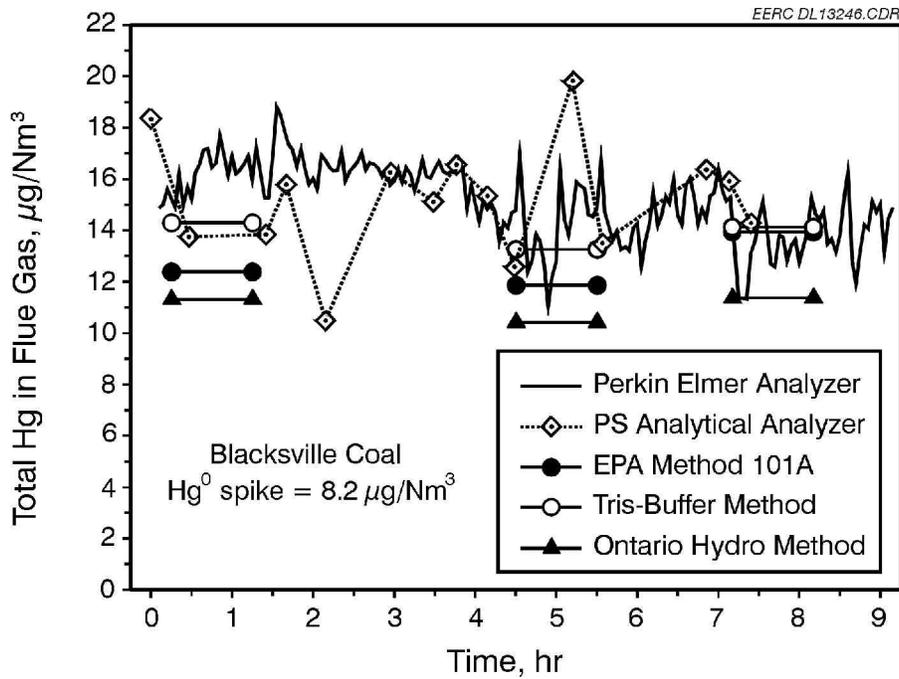


Figure 20. Comparison of CEMs to impinger-based mercury-sampling methods as a function of time (Blacksville coal and Hg⁰ spiking at the baghouse outlet).

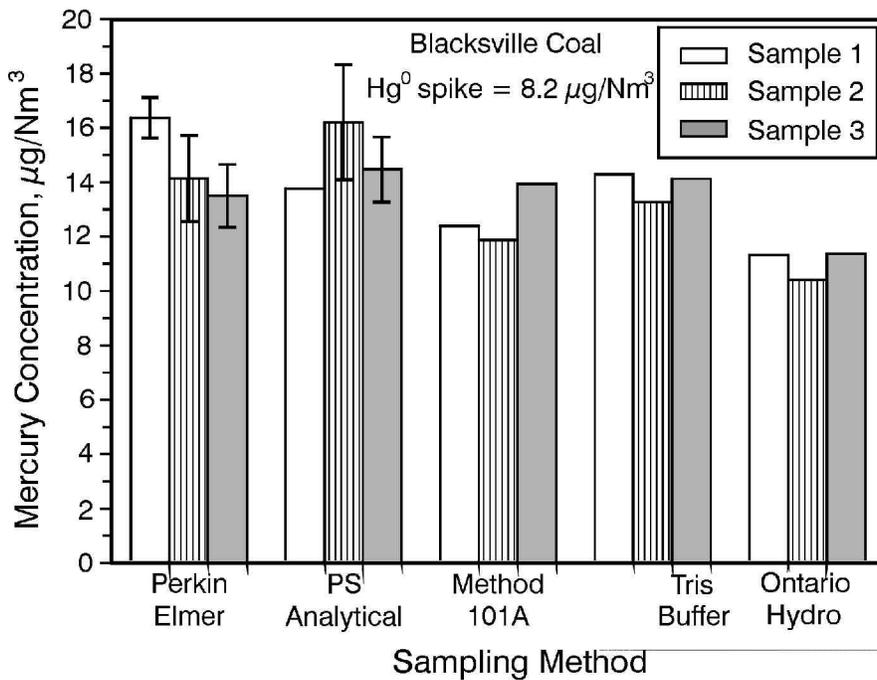


Figure 21. Comparison of CEMs during the sampling period of the impinger-based methods (Blacksville coal and Hg⁰ spiking at the baghouse outlet).

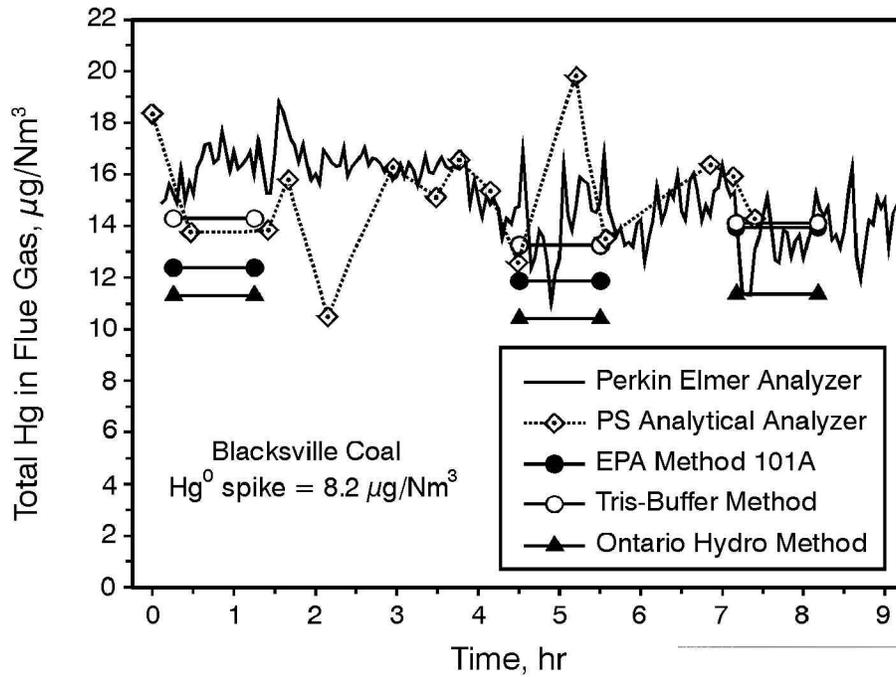


Figure 22. Comparison of CEMs to impinger-based mercury-sampling methods as a function of time (Blacksville coal and spiking $HgCl_2$ at the baghouse outlet).

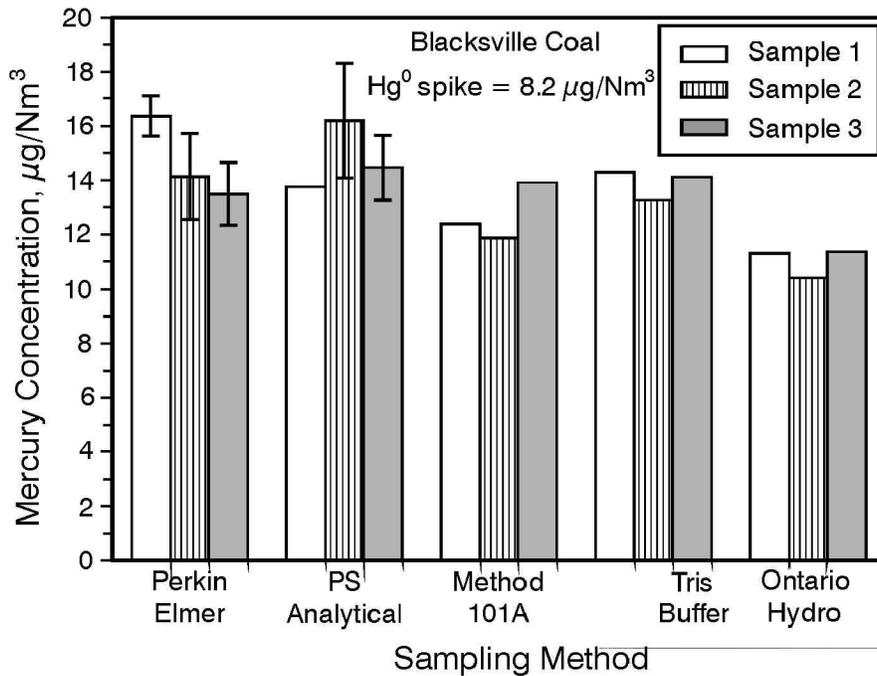


Figure 23. Comparison of CEMs during the sampling period of the impinger-based methods (Blacksville coal and $HgCl_2$ spiking at the baghouse outlet).

Conclusions and Observations

- It appears that some fly ashes can catalyze mercury oxidation, thereby having a substantial effect on mercury speciation. The fly ash effect was significant for tests with Blacksville coal and less pronounced for tests with the two subbituminous coals.
- All impinger-based methods, if done right, show good agreement for measuring total mercury. EPA Method 29 and EPA Method 101A have been validated for total mercury.
- EPA Method 29 does not speciate mercury correctly in all cases. It appears that high levels of SO₂ (>1500 ppm) is part of the cause.
- Both the tris-buffer and Ontario Hydro methods are promising mercury speciation methods.
- A very high level of quality control and quality assurance is necessary to consistently obtain good mercury data in flue gas studies.
- The MESA method appears to overestimate Hg²⁺ at SO₂ concentrations of >500 ppm in combustion processes. The most likely cause is an interaction between SO₂ and NO_x in the first sorbent trap.
- The Ontario Hydro and tris-buffer methods both require addition of a preservative immediately after sampling to stabilize the Hg²⁺ in solution. For the Ontario Hydro method, KMnO₄ solution is used. For the tris-buffer method, H₂O₂ solution is used.
- The RTI methods test results to date have been inconclusive.
- The Perkin Elmer MERCEM and P.S. Analytical Sir Galahad mercury analyzers gave results for total mercury that were within 15%–25% of the impinger-based methods during the EERC pilot-scale tests.

Research Recommendations

- A much better understanding of the chemistry, thermodynamics, and kinetics of mercury in combustion systems is needed to better develop measurement methods and control strategies.
- Research is needed to determine the mechanism of the mercury–fly ash interactions.
- The role of Cl₂/HCl in mercury speciation appears to be important. However, research needs to be done to better develop a method to speciate between the two forms of chlorine in combustion systems. It appears that EPA Method 26A does not speciate Cl₂/HCl correctly when high levels of SO₂ are present.

- Although the MESA method and EPA Method 29 appear to overestimate Hg²⁺ under certain conditions, it is important to more fully evaluate what these conditions are. A substantial amount of mercury speciation data have been reported based on these methods. Therefore, the validity of these data needs to be determined.
- More development work should be done with the MESA method, since it is simple and easy to use. It does not appear that the problems with the method are insurmountable if more research is done.
- Evaluate the effect of the sample filter temperature and configuration on particulate mercury capture and mercury conversion.
- Formally validate a mercury speciation method.
- More development and testing are needed for mercury CEMs. The analytical techniques seem to be fairly well developed, but the getting the mercury from the combustion system to the analyzers needs more work.
- A mercury CEM needs to be developed to speciate mercury in flue gas streams from combustion sources.

Contract Information

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