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# BENCH- AND PILOT-SCALE EVALUATION OF MERCURY SPECIATION

## MEASUREMENT METHODS

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## **INTRODUCTION**

The 1990 Clean Air Act Amendments require the U.S. Environmental Protection Agency (EPA) to assess the health risks associated with mercury. Since the rate of mercury deposition and the type of control strategies used may depend on the type of mercury species emitted, a proven sampling method that can reliably and accurately speciate mercury at the very low concentrations found in coal combustion flue gas is necessary. A number of mercury speciation methods have been proposed, including wet-chemistry methods, such as EPA Method 29, the Ontario Hydro method, and the tris-buffer method, as well as dry methods such as the Mercury Speciation Absorption Method (MESA). In addition, a number of companies are developing continuous emissions monitors to speciate mercury by difference. Bench- and pilot-scale tests, sponsored by the Electric Power Research Institute (EPRI) and the U.S. Department of Energy (DOE), are currently under way at the Energy & Environmental Research Center (EERC) to determine the most accurate and precise mercury speciation method available.

## **OBJECTIVES**

The overall objective of the test program is to determine whether EPA Method 29 or other sampling methods can reliably quantify and speciate mercury in flue gas from coal-fired boilers at both the inlet and outlet of a particulate control device such as a pulse-jet baghouse. A specific goal of the project is to determine the precision and bias of the various mercury speciation methods as a function of process variables.

## **SCOPE OF WORK AND EXPERIMENTAL APPROACH**

Previous pilot-scale tests at the EERC showed that when elemental mercury ( $\text{Hg}^0$ ) was spiked into the flue gas, part of the  $\text{Hg}^0$  spike was measured as "oxidized" mercury using EPA Method 29.<sup>1</sup> It was uncertain whether the apparent conversion of  $\text{Hg}^0$  to  $\text{Hg}^{+2}$  was occurring in the flue gas stream prior to sampling or in the peroxide impingers of EPA Method 29. A series of four bench-scale test matrices have been completed, and several more pilot-scale tests are currently under way to try to answer this

question. Several mercury speciation methods have been tested at the bench and/or pilot scale. The methods tested include the following:

- EPA Method 29
- Ontario Hydro method
- Acetate buffer method
- Tris-buffer method
- Mercury Speciation Adsorption (MESA) method
- Method 101A (used as a reference for total mercury)

A description of each of the sampling methods is given below.

*EPA Method 29 (multimetals sampling train).* EPA Method 29 uses seven impingers. The first impinger is empty and acts as a moisture knockout chamber. Impingers 2 and 3 contain 10% hydrogen peroxide in a 5% nitric acid solution, which, according to speculation, capture  $\text{Hg}^{+2}$  and other trace metals. The fourth impinger is dry to prevent mixing of the two types of impinger solutions. The remaining mercury, which is thought to be elemental mercury, is captured in the fourth and fifth impingers. Impingers 4 and 5 contain 4% potassium permanganate dissolved in a 10% sulfuric acid solution. The last impinger contains silica gel to ensure the flue gas is thoroughly dried before it enters the dry gas meter. After the sampling is completed, the solutions are prepared and analyzed for mercury using cold-vapor atomic absorption.

*Ontario Hydro method.* This method, which was developed by Keith Curtis of Ontario Hydro, is a modification of EPA Method 29.<sup>2</sup> The two acidified peroxide impingers of EPA Method 29 are replaced by two impingers containing 1 N potassium chloride (KCl) dissolved in deionized water. The advantages of this method are that it eliminates some of the difficulties that occur during preparation of the peroxide solution for analysis and avoids the possible sulfur dioxide ( $\text{SO}_2$ ) interference in mercury speciation that may affect EPA Method 29.

*Acetate buffer method.* This method, which was developed by Radian Corporation, is also a modified EPA Method 29. The first empty impinger of EPA Method 29 is replaced with a buffer solution of 1 N sodium acetate solution dissolved in acetic acid. The purpose of the buffer is to remove  $\text{SO}_2$  and "oxidized" mercury in an attempt to eliminate possible interference from  $\text{SO}_2$  in the measurement of "oxidized" mercury in the peroxide solutions of EPA Method 29.

*Tris-buffer method.* The tris-buffer method was also developed by Radian Corporation. For the bench-scale tests, the sampling train consisted of a tris-buffer impinger, two hydrogen peroxide impingers, and two potassium permanganate impingers. The tris-buffer solution consists of tris (hydroxymethyl) aminomethane and ethylenediaminetetraacetic acid (EDTA) dissolved in water. The EDTA acts as a chelating agent and allows the tris buffer to absorb more  $\text{SO}_2$  without breakthrough. After the bench-scale tests were completed, it was learned that Radian had modified the tris-buffer method by eliminating the hydrogen peroxide impingers and using only two tris-buffer impingers and two potassium permanganate impingers. This is the configuration that is currently being used in the pilot-scale tests. The peroxide impingers were removed because Radian believes that the peroxide impingers may collect some elemental mercury, while not removing all of the "oxidized" mercury.

**MESA method.** The MESA method, as developed by Frontier Geosciences, Inc., uses solid sorbents to speciate mercury during sample collection.<sup>3</sup> The first sorbent collects  $\text{Hg}^{+2}$  using a mixture of potassium hydroxide (KOH), calcium oxide lime, and KCl. This is followed by iodine-impregnated activated carbon, which collects the  $\text{Hg}^0$ . The sampling train is operated at approximately 95°C to prevent water condensation and the flow rate through the sorbent traps is approximately 0.5 L/min. In the laboratory, the KCl-lime and iodated carbon traps are digested and strong acid-leached. The digests are analyzed for mercury using cold-vapor atomic fluorescence spectroscopy.

**EPA Method 101A.** This EPA reference method measures total mercury in a flue gas stream. Three impingers of the same acidified potassium permanganate solution described above for EPA Method 29 and a silica gel impinger are used in this method.

### Pilot-Scale Tests

The EERC pilot-scale furnace, known as the particulate test combustor (PTC), is a 550,000-Btu/hr pulverized coal-fired boiler designed to generate fly ash representative of that produced in a full-scale utility boiler. System temperatures, pressures, flow rates, flue gas constituent concentrations ( $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ , and  $\text{NO}_x$ ), and baghouse operating data are monitored continuously using the PTC instrumentation and downloaded to a data acquisition system. The pulse-jet baghouse is a 20-in.-ID chamber that is heat-traced and insulated. The combustor produces approximately 200 acfm of flue gas at 350°F; therefore, three 13-ft by 5-in. woven glass (22-oz/yd<sup>2</sup>) bags provide an air-to-cloth ratio of 4.2 ft/min. The bags are cleaned individually on timed intervals using a 60-psi air pulse.

Fourteen pilot-scale tests have been completed. Tests 1 through 4 evaluated EPA Method 29 using the criteria of EPA Method 301; these have been reported previously.<sup>1</sup> For the next series of ten tests, five mercury measurement methods were tested: EPA Method 29, the Ontario Hydro method, the acetate buffer method, the MESA method, and EPA Method 101A. The inlet and outlet piping of the pulse-jet baghouse was designed so that four methods could be used simultaneously. Two coals were tested: a Blacksville bituminous coal from the Pittsburgh No. 8 seam and an Absaloka subbituminous coal from the Powder River Basin. Both baseline and tests with elemental mercury spiking of the flue gas were completed for each coal. In addition, the methods were also compared with the PTC fired on natural gas, both with and without  $\text{Hg}^0$ ,  $\text{SO}_2$ , hydrogen chloride (HCl), and ash injection.

### Bench-Scale Tests

A bench-scale test system was designed and built to simulate flue gas conditions. Elemental mercury vapor ( $\text{Hg}^0$ ) or mercury(II) chloride ( $\text{HgCl}_2$ ) vapor was introduced into the system by flushing nitrogen around calibrated permeation tubes. The quantity of mercury vapor released into the simulated flue gas stream was determined by its vapor pressure at a specific temperature, which was controlled by using a straight-tube condenser and water bath. The quantity of mercury vapor is also checked regularly using EPA Method 101A. All components of the bench-scale system are either Teflon, Teflon-lined or glass.

Four bench-scale test matrices have been completed. The first three test matrices were set up as full-factorial designs, and the fourth test matrix was a  $2^{5-1}$  fractional factorial design. Each test series was repeated to provide two data points for each sampling method tested at each test condition. The primary purpose of Test Series I was to determine what caused the observed differences between EPA

Method 29 and the MESA method during the first series of pilot-scale tests. The primary variables were  $\text{SO}_2$  (0 and 1500 ppm),  $\text{HCl}$  (0 and 50 ppm), and mercury species ( $\text{Hg}^0$  or  $\text{HgCl}_2$ ). The mercury concentration was  $20 \mu\text{g}/\text{m}^3$ . The composition of the baseline simulated flue gas was 4%  $\text{O}_2$ , 15%  $\text{CO}_2$ , 10%  $\text{H}_2\text{O}$ , with the balance nitrogen. The purpose of Test Series II and III was to determine which flue gas constituents cause the apparent conversion of elemental to "oxidized" mercury observed in the pilot-scale tests. The effects of  $\text{Cl}_2$  (0 and 10 ppm),  $\text{NO}_x$  (0 and 600 ppm), and fly ash (none or Blacksville) were evaluated using EPA Method 29 and the MESA method. For these two test series, 1500 ppm  $\text{SO}_2$ , 50 ppm  $\text{HCl}$ , and  $20 \mu\text{g}/\text{m}^3 \text{Hg}^0$  were added to the baseline simulated flue gas from Test Series I.

The purpose of Test Series IV was to evaluate the effect of  $\text{SO}_2$  (0 and 1500 ppm),  $\text{HCl}$  (0 and 50 ppm),  $\text{NO}/\text{NO}_2$  (0/0 and 600 ppm/30 ppm),  $\text{Cl}_2$  (0 and 10 ppm), and fly ash (none or Blacksville) on the tris-buffer and Ontario Hydro methods. The composition of the baseline simulated flue gas was 4%  $\text{O}_2$ , 15%  $\text{CO}_2$ , 10%  $\text{H}_2\text{O}$ , and  $20 \mu\text{g}/\text{m}^3 \text{Hg}^0$ , with the balance nitrogen. In addition, several tests were completed to evaluate the effect of  $\text{Cl}_2$  concentration (1, 3, 5 and 10 ppm) on mercury speciation using EPA Method 29 and the tris-buffer method.

## RESULTS

### Pilot-Scale Tests

The results from the method comparison tests firing natural gas, Blacksville coal, and Absaloka coal are shown in Figures 1 through 3. There was very good agreement for total mercury among all the methods for the natural gas test when only  $\text{Hg}^0$  was spiked into the flue gas, and nearly all the mercury was reported as elemental for each of the four speciation methods. The data were more variable when

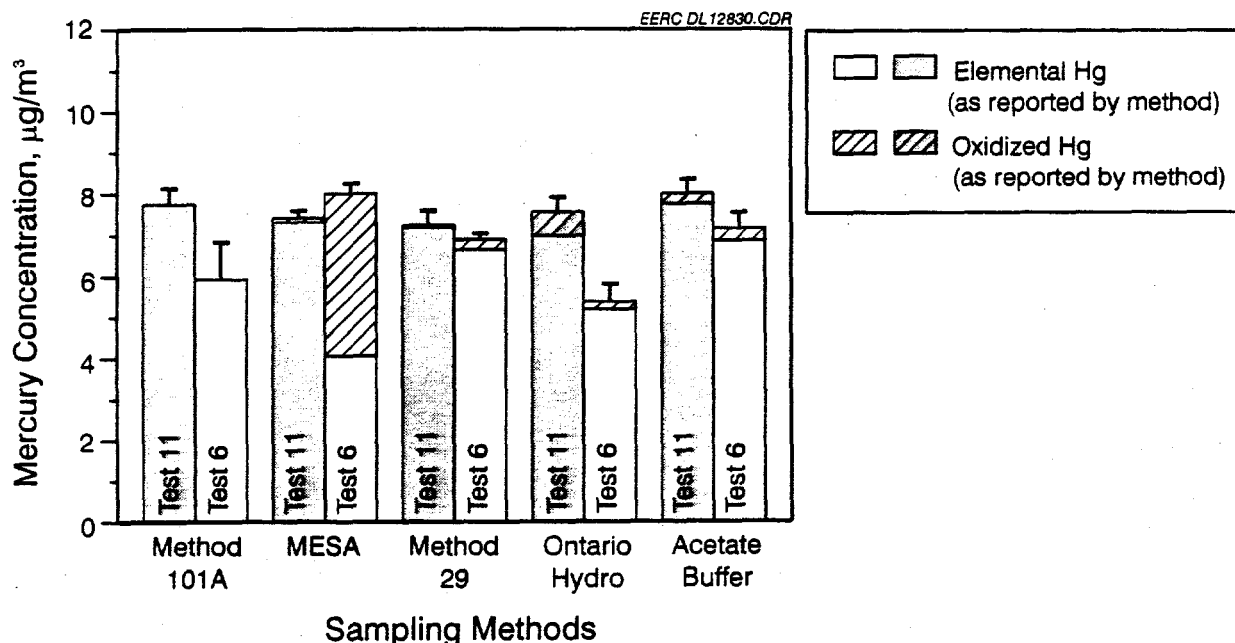


Figure 1. Comparison of mercury speciation sampling methods firing natural gas (error bars are for total mercury). Test 6 has  $\text{Hg}^0$  at  $6.0 \mu\text{g}/\text{m}^3$ ,  $\text{SO}_2$  at 1700 ppm, and  $\text{HCl}$  at 50 ppm spiked into flue gas. Test 11 has only  $\text{Hg}^0$  at  $8.5 \mu\text{g}/\text{m}^3$  spiked into flue gas.

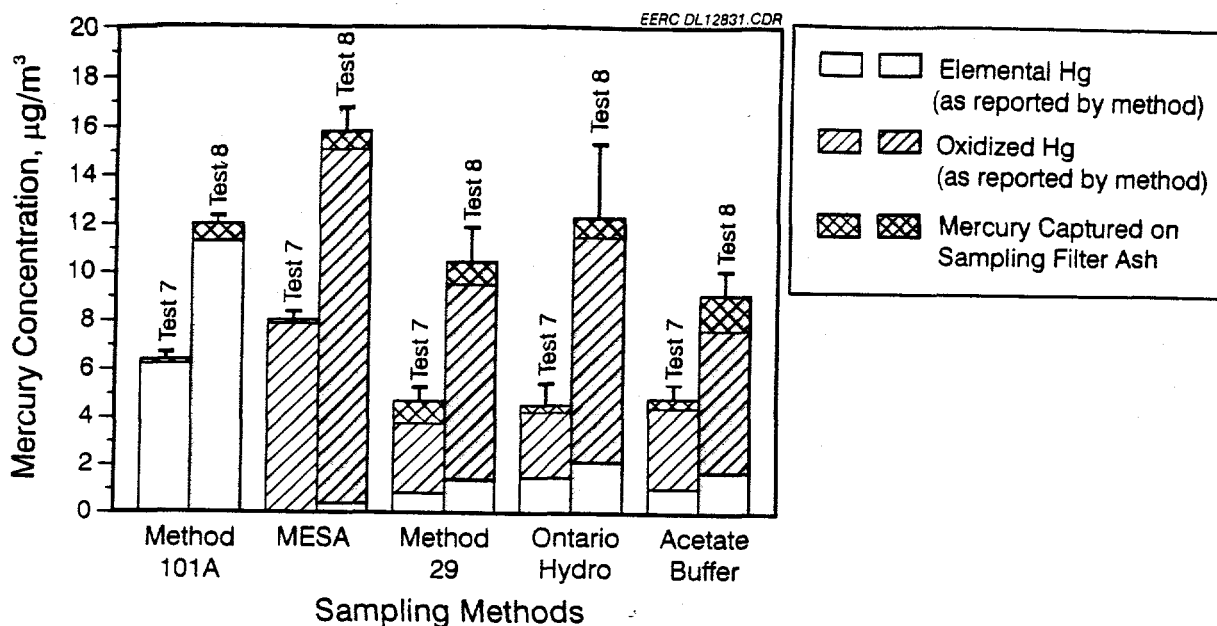


Figure 2. Comparison of mercury speciation sampling methods firing Blacksville bituminous coal (error bars are for total mercury). Test 7 is a baseline test. Test 8 has an additional  $7.0 \mu\text{g}/\text{m}^3$   $\text{Hg}^0$  spiked into the flue gas.

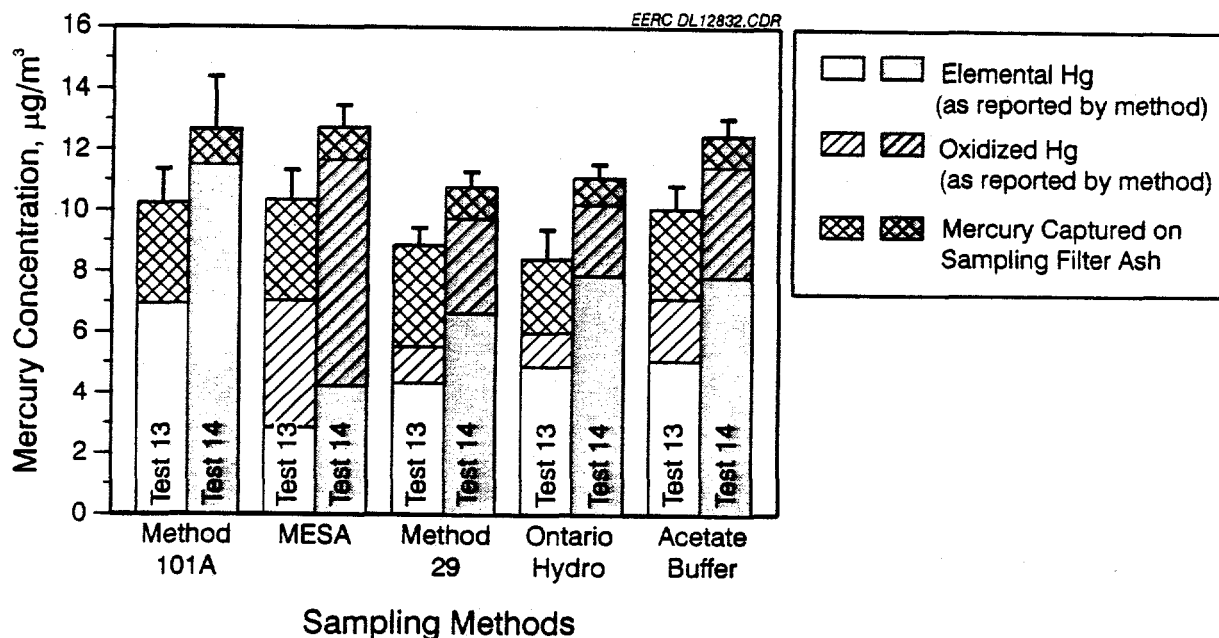


Figure 3. Comparison of mercury speciation sampling methods firing Absaloka subbituminous coal (error bars are for total mercury). Test 13 is a baseline test. Test 14 has an additional  $7.1 \mu\text{g}/\text{m}^3$   $\text{Hg}^0$  spiked into the flue gas.



1700 ppm SO<sub>2</sub> and 50 ppm HCl were added to the flue gas in addition to the elemental mercury spike. For EPA Method 29, the acetate buffer method, and the Ontario Hydro method, about 90% of the injected elemental mercury was measured as elemental mercury. However, the MESA method collected nearly 50% of the elemental mercury spike in the first sorbent trap indicating "oxidized" mercury. These results are shown in Figure 1.

Results from tests firing Blacksville and Absaloka coals (Figures 2 and 3) showed that a significant portion of the elemental mercury flue gas spike was converted to oxidized mercury for all the mercury speciation methods, with the MESA method again measuring a much higher percentage as oxidized. Based on the pilot-scale results, more fundamental bench-scale studies were initiated to determine which flue gas constituents affect mercury speciation. The remainder of this paper will focus on the bench-scale test results.

### Bench-Scale Tests

The statistical analysis of the bench-scale data was based on the amount of mercury reported as elemental as a percentage of the total mercury measured by the method. Analysis of the data from Test Series I, II, and III showed that Cl<sub>2</sub> had a major effect on mercury speciation using EPA Method 29. Up to 50% of the elemental mercury was collected in the peroxide solution when 10 ppm Cl<sub>2</sub> was added. The results also showed that SO<sub>2</sub> and fly ash decreased the amount of Hg<sup>0</sup> that was collected in the permanganate solution. When 1500 ppm SO<sub>2</sub> was added, 10%–20% of the elemental mercury was reported as "oxidized." A small effect was observed for NO<sub>x</sub>. The effects of hydrogen fluoride and HCl were not statistically significant.

For the MESA method the statistical analysis of the data from Test Series I, II, and III showed that SO<sub>2</sub> had only a small effect and the effects of chlorine and HCl were not statistically significant. However, NO<sub>x</sub> had an overwhelming effect on mercury speciation using the MESA method. Up to 95% of the mercury was collected in the KCl-KOH-lime trap, and therefore was reported as "oxidized" mercury. Previous work at the EERC and at the DOE Pittsburgh Energy Technology Center (PETC) has shown that sodium-based SO<sub>2</sub> sorbents in the presence of SO<sub>2</sub> and water can convert NO to NO<sub>2</sub> at 95°C, which is the temperature at which the MESA sampling train is operated.<sup>4,5</sup> Therefore, it is possible that the same effect is occurring in the potassium-based trap of the MESA method, with the NO<sub>2</sub> oxidizing Hg<sup>0</sup> to Hg<sup>+2</sup>. The conversion of NO to NO<sub>2</sub> is highly dependent on temperature and is not observed below 65°C or above approximately 150°C.

To determine whether NO<sub>x</sub> alone was responsible for the large effect on the MESA method or SO<sub>2</sub> must also be present, two MESA tests were piggy-backed onto Test Series IV. The tests were performed by taking a slipstream of the flue gas just prior to the tris-buffer or Ontario Hydro sample trains. For the tests with only 600 ppm NO and 30 ppm NO<sub>2</sub>, virtually 100% of the mercury was reported as elemental mercury. However, when 1500 ppm SO<sub>2</sub> was added to the simulated flue gas, only 36% of the mercury was reported as elemental. This provides an explanation for previous pilot-scale results where the mercury speciation reported using the MESA method agreed with EPA Method 29 only for a natural gas test where no SO<sub>2</sub> was added.

The statistical analysis of the data from Test Series IV for the tris-buffer method showed that chlorine had the largest effect, followed by Blacksville fly ash. Approximately 20% of the elemental

mercury was collected in the peroxide solution when 10 ppm chlorine was added to the simulated flue gas. However, it is unknown to what extent chlorine exists in the flue gas at temperatures of 150°–175°C. Smaller effects were observed for NO/NO<sub>2</sub> and SO<sub>2</sub>, and the effect of HCl was not statistically significant. Similar analysis of the Ontario Hydro data showed that chlorine had the largest statistically significant effect, followed by SO<sub>2</sub>, fly ash, and NO/NO<sub>2</sub>. Up to 80% of the elemental mercury was collected in the KCl solutions and, therefore, reported as "oxidized" mercury when 10 ppm chlorine was added. Again, the effect of HCl was not statistically significant. The most interesting result was the very large positive interaction between SO<sub>2</sub> and chlorine. The SO<sub>2</sub> appears to mitigate the effect of chlorine when fly ash is not present. This may be the result of HCl formation in the KCl impingers in the presence of SO<sub>2</sub>.

## PRELIMINARY OBSERVATIONS

The following are preliminary observations from the bench-scale tests that have been completed to date:

- For EPA Method 29, up to 50% of the Hg<sup>0</sup> is collected in the peroxide solution when 10 ppm chlorine is added, and 10%–20% is collected in the peroxide solution when 1500 ppm SO<sub>2</sub> is added.
- The mercury speciation ability of the MESA method is not affected by SO<sub>2</sub>, HCl, or chlorine; however, NO<sub>x</sub> in the presence of SO<sub>2</sub> has a significant impact.
- Addition of 10 ppm chlorine had the largest effect on both the tris-buffer and Ontario Hydro methods. Approximately 20% of the elemental mercury was reported as "oxidized" for the tris-buffer method and up to 80% was reported as "oxidized" for the Ontario Hydro method.
- Addition of 1500 ppm SO<sub>2</sub> had only a small effect (~5%) on mercury speciation using the tris-buffer and Ontario Hydro methods.

## FUTURE WORK

The continuing focus of the project is to identify a sampling method that can reliably speciate mercury in flue gas from coal combustion at both the inlet and outlet of a particulate control device. A series of five more weeks of pilot-scale tests is currently under way. The objectives of the tests are to compare mercury speciation using the tris-buffer and the Ontario Hydro methods. The flue gas will be spiked with Hg<sup>0</sup> or HgCl<sub>2</sub>. Several continuous mercury emission monitors will also be available during the tests. Two weeks of shakedown and natural gas pilot-scale tests were recently completed. Three additional weeks of pilot-scale tests are planned with Blacksville, Absaloka, and Comanche coals. When the most promising mercury speciation method is identified, an EPA Method 301 validation will be completed, with additional pilot-scale tests using flue gas spiking to determine the precision and bias of the method.

An extensive report on the state of the art for mercury-sampling methods, including wet and dry chemistry, as well as continuous emissions monitors, is currently being prepared. Objectives of the report are to include mercury measurement data from as many facilities as possible and to use the data to evaluate the mercury speciation ability of various measurement methods.

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