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## SAMPLING AND ANALYTICAL METHODS – IMPROVING SORBENT TRAPS FOR MERCURY SPIKE RECOVERY TO MEET EPA METHOD APPENDIX K CRITERIA

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### ***Project Description***

A critical issue affecting EPA Method 324 is spike recovery. While other quality assurance/quality control (QA/QC) tests such as duplicate Method 324 traps and comparison with Ontario Hydro (OH) sampling show that Method 324 has merit as a total mercury-sampling method (1), the ability to recover mercury from the spike trap is troublesome, and this is an important QA measure. This project will investigate different spiking methods guided by an experienced understanding of flue gas–mercury–carbon interactions. In addition, various zeolites will be evaluated as possible alternative sorbents for this method.

### ***Goal***

To compare traps spiked using a chemisorption technique with those using the current spiking technique (exposure to mercury in an inert gas for a known time). Impregnated zeolites (with selenium or other metals and inorganic compounds) will be evaluated to determine their effectiveness to capture mercury in a bench-scale testing system as a possible means of improving this method.

### ***Rationale***

Method 324 is designed for the continuous sampling of total mercury emissions in combustion flue gas streams. The operating principle for this test method is to draw flue gas through three carbon traps connected in series. The first trap is the primary sample, while the second trap is used to determine whether the first trap broke through during testing. The third trap in this series is spiked with elemental mercury as a QA method for checking the retention and ability to analyze the mercury on the first trap. After exposure to flue gas, the carbon traps are digested individually and submitted for analysis by cold-vapor atomic fluorescence spectrometry (CVAFS).

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mercury sample method, the ability to recover mercury from the spike trap is troublesome as it is an important QA measure.

Processes currently used to spike these traps involve passing an inert gas seeded with mercury from a well-characterized permeation source for a known time. Upon exposure to flue gas, this mercury, which is physisorbed onto the carbon, is almost completely liberated by the flue gas components which seek to chemically bond with the carbon structure.

Bench-scale mercury sorption tests and XAFS (x-ray atomic fluorescence spectroscopy) spectra of flue gas-exposed sorbents indicate that the nature of the sorption mechanism for mercury on carbon is chemical in the presence of halogens and involves the formation of organomercury bonds (2). Sorption of elemental mercury in air at low temperatures is primarily physical in nature, depending on the sorbent, and, therefore, unstable in the flue gas environment.

Spiking of the carbon trap in the Method 324 test for total mercury should be based on the current understanding of the carbon–mercury interaction. This model, developed by Edwin Olson of the EERC, is based on over 2000 bench-scale sorbent fixed-bed tests and years of field observation. It predicts that a carbon treated with a halogen would provide the chemically active sites necessary for mercury retention during the exposure period in the Method 324 test. This could be accomplished in several ways. Mercury in a simulated flue gas could be loaded onto a Method 324 trap in a simulated flue gas. This could then be purged and used as a spike during actual testing. Similarly, the mercury can be added to a trap where the carbon has been treated with a halogen. Still, another possible solution to this problem could be spiking the trap with a liquid standard of  $\text{HgCl}_2$ .

The outcome of these alternative techniques to spiking the Method 324 trap is that the spiked mercury would be retained using the same mechanism binding the sampled mercury in the sample traps: chemisorption.

## ***Approach***

### **Improving Mercury Spike Recovery in EPA Method Appendix K Carbon Traps**

This project will verify that physisorption is the cause for unfavorable spike recovery in the Method 324 tests by performing bench-scale tests on a series of carbon and impregnated carbon sorbents. These tests are roughly outlined below:

1. Loading mercury using nitrogen gas only (Method 324), followed by exposure to synthetic flue gas without mercury while monitoring the output of the fixed bed.
2. Loading mercury using conditions favoring chemisorption (a combination of water,  $\text{NO}_2$ ,  $\text{HCl}$ , and  $\text{Hg}$  at  $150^\circ\text{C}$ ), followed by synthetic flue gas without mercury.
3. Loading mercury using a liquid (acidic solution of  $\text{Hg}^{2+}$ ) on carbon followed by exposure to synthetic flue gas without mercury.

At the end of each test, samples will be submitted for analysis by acid digestion followed by CVAFS or cold-vapor atomic absorption (CVAA). In this way, a spiking method based on chemisorption can be explored as an alternative to physisorption of elemental mercury on the sorbent.

### Impregnated Zeolites as Specialized Mercury Sorbents

Gram-scale samples of selenium- and sulfur-loaded zeolites will be prepared. Up to three zeolites will be selected based on their channel diameters, and introduction of the selenium and sulfur into the zeolites will be performed following preparation methods described in the literature. The amount of element loaded will be characterized by either XAFS analysis or wet chemical analysis.

### Experimental Apparatus

A mercury permeation source is used to load sorbent traps with a known mass of mercury (in the case of physisorbed and chemically treated sorbent traps), as shown in Figure 1. This permeation source is monitored with a mercury analyzer between loadings to verify the permeation rate of the source. During loading, the analyzer pulls the mercury vapor/nitrogen through the trap. In the unlikely event that mercury breaks through the trap during the loading process, the instrument will detect this breakthrough.

After several sorbent traps have been loaded, they are evaluated with a synthetic flue gas of known concentrations of component gases. A secondary trap is occasionally used to capture mercury liberated from the first trap. These tests are conducted with the traps at temperatures between 220° and 275°F. A four-port manifold allows four traps to be exposed simultaneously. The inlet side of each trap is connected to one of the ports, while the outlet is connected to a sampling system similar to those used in Method 324 field testing. The flue gas is pulled through the trap at 500 sccm and the volume of gas determined with a sampling system commonly employed for Method 324 testing. A desiccant-filled impinger is used to dry the gas before it reaches the sampling system.

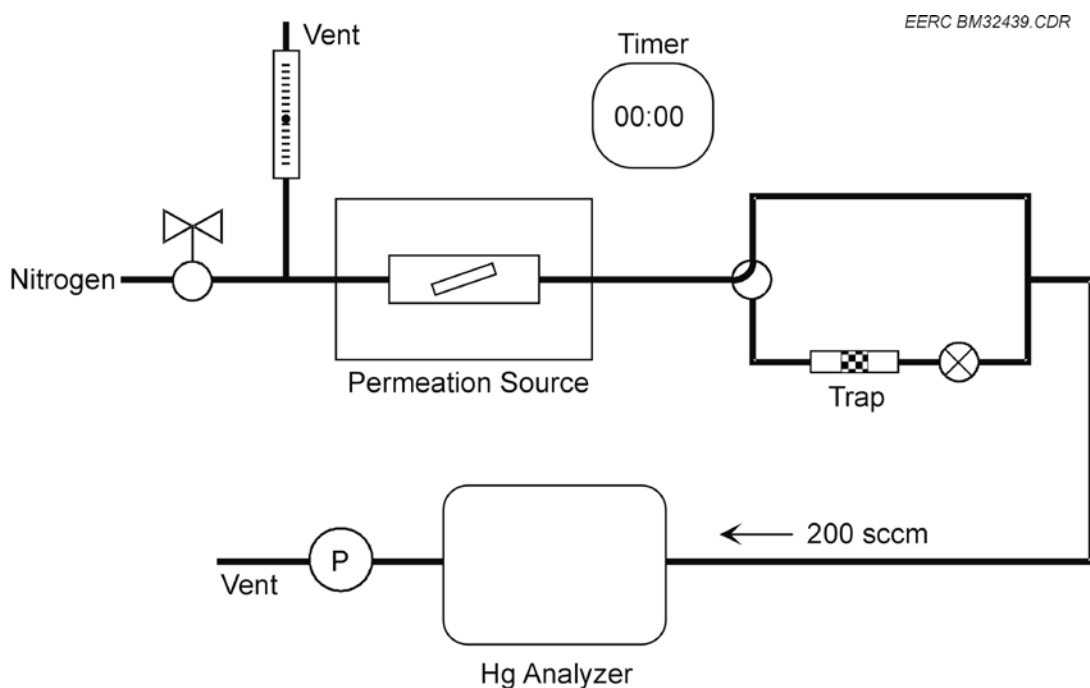


Figure 1. Apparatus for loading traps via permeation source.

Traps are made by necking down the middle section of a 6-inch-long piece of 10-mm-o.d. pyrex tubing. This tube is then separated at the necked-down section to make two trap tubes, 3 inches in length. The edges of these small tubes are fire-polished and then allowed to cool. Quartz wool is balled up and inserted into a sorbent trap tube. This is weighed before adding between a 0.5- and 1-cm column of sorbent. The trap is weighed again to determine the mass of sorbent. After this, a similar quartz wool ball is inserted to contain the sorbent in the trap (see Figure 2).

### Work Plan

#### Improving Mercury Spike Recovery in EPA Method Appendix K Carbon Traps

Two carbons, subjected to different pretreatment and spiking methods are used in this project. The first is a nitrogenated coconut shell-based carbon from OhioLumex, the same used in commercially available Method 324 traps. The second is an unactivated carbon from Calgon (F400<sup>®</sup>) sieved to -20 mesh.

Traps made with these carbons are loaded by one of several methods: exposing to Hg permeation source gas for a known time; insipient loading of an acidic liquid Hg<sup>2+</sup> standard; and activating with a liquid or gas followed by exposure to a Hg permeation source.

To test these traps, the apparatus described is used to control the exposure of said traps to synthetic flue gas that contains no gaseous Hg. The components of this flue gas are listed in Table 1.

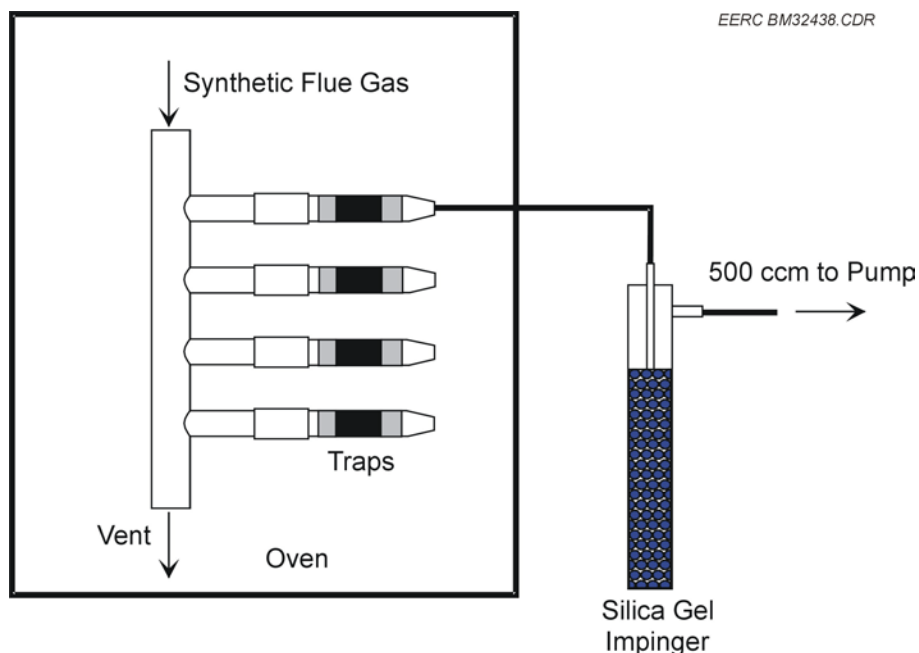


Figure 2. Apparatus for evaluating spiked carbon traps. Only one trap is shown, with additional plumbing, for clarity.

**Table 1. Flue Gas Constituents Used for Evaluations**

Gas	Concentration
O <sub>2</sub>	6%
CO <sub>2</sub>	12%
H <sub>2</sub> O	8%
SO <sub>2</sub>	1600 ppm
NO	400 ppm
HCl	Off
NO <sub>2</sub>	20 ppm
N <sub>2</sub>	Balance

Sample sets consist of the spiked traps themselves, backup “catch traps” if used, as well as a similarly spiked control trap that had not been exposed to flue gas. These sample sets are submitted to the EERC Analytical Research Laboratory (ARL) in digestion bottles for total mercury determination. A typical trap loading of 500 ng was chosen as a representative loading for a Method 324 trap.

### **Impregnated Zeolites as Specialized Mercury Sorbents**

Using specially prepared impregnated sorbents according to methods outlined in literature, determination of the sorbent capacity will be performed using the same bench-scale mercury-testing system, using a synthetic gas mixture to simulate the flue gas of a boiler firing a bituminous coal. The gas mixture containing known mercury concentrations will flow through a packed bed of the sorbents for given times, after which the amount of mercury sorbed will be determined. Limited tests with sorbent samples previously spiked with known amounts of mercury will also be made to evaluate spike retention on the sorbents. Analysis of the amount of sorbed mercury will be performed either with a method similar to that for Appendix K carbon traps or by digestion, depending on what properties the sorbents are found to have. Appropriate blanks, replicate samples, and standards will be used to assure the quality of the results.

### ***Progress***

Initial testing attempted to demonstrate the failure of a physisorbed spike. These tests showed no such effect. In other words, traps using unadulterated carbon loaded with the permeation source method were subjected to the full flue gas matrix (including HCl at 50 ppm) and did not lose the spiked amount. The source of this effect was quickly determined to be the presence of HCl in the gas at a concentration of 50 ppm.

In practice, a spike trap is placed downstream of the sample trap. The gas seen at the spike trap contains little HCl because of the capture of HCl in the sample trap. This was verified using a Thermoelectron 15C HCl analyzer to measure the breakthrough of HCl from a typical Method 324 trap. The time to 50% of inlet HCl was approximately 1 hour.

Tests were repeated without HCl, and the spike failure effect was found to occur. Testing is currently taking place, and data are becoming available for analysis and reporting.

In the second task, the appropriate zeolites were secured and are presently being impregnated for testing in 2008.

### *Quality Assurance/Quality Control*

#### **Quality Objectives**

1. To use procedures that ensure a mass balance for mercury of better than  $\pm 10\%$  can be determined for all experiments. This metric will be determined by collecting the gas from spiked traps with a chemically activated sorbent or Method 101A train or activated carbon catch trap. This mercury will be analyzed to quantify evolved mercury along with the spike test trap itself. Analysis will be done through the ARL using established procedures for collecting and analyzing mercury.
2. To ensure bench-scale gas is generated correctly, bench-scale procedures including the calibration of individual flowmeters and controllers will be followed. The metric for this quality objective will be the calibration data themselves as compared to historical data. Slopes for flowmeter and controller calibrations should be within  $\pm 5\%$  before and after these experiments.
3. For preparation of the zeolites with selenium and sulfur, the metric for this quality objective is that the loading can be performed consistently with loadings equal to or greater than those reported in the literature.
4. Impregnated zeolite sorbents will demonstrate superior spike retention and recovery. The metric for this quality objective is that reproducible spike recoveries of  $\pm 10\%$  (half that allowed for carbon traps) can be obtained.

#### **Measurement/Data Acquisition**

Measurement and data acquisition, except in the case of the mercury analyzer, are performed mainly by reading digital displays and recording values, namely mass and temperature. Bench-scale thermal mass flow controllers are calibrated using a Gilibrator, a bubble-type flowmeter that is itself a National Institute of Standards and Technology (NIST)-traceable standard.

#### **Assessment and Validation**

The degree of failure of the spike trap is determined by the amount of loaded mercury that was liberated after exposure to flue gas. Data will be analyzed and reported according to these percent losses of mercury. A trap preparation and loading method that results in more than 10% loss of mercury will be interpreted as failing. 10% loss was chosen because of the loading and measurement uncertainties involved.

### *Status*

This project is in the sample-generating and data-collecting phase.

## ***Potential Applications and Benefits***

### **Potential Users and Real-Life Applications**

Power plants, companies that provide Method 324 traps, and research organizations are the potential users of the results generated by this project.

### **Technology Transfer**

Technology could be transferred to businesses that construct Method 324 traps.

### **Technical and Economic Benefits**

Improving QA/QC for any measurement system has inherent technical and economic benefits. Enhancing the reliability of this procedure will increase the use of this cost-effective means of measuring mercury.

### **Environmental and/or Health Benefits**

Method 324 will most likely become the routine method power plants use to monitor and report mercury output. The toxicity of mercury is well known. Power plants are a major source of anthropogenic mercury in the United States.

## ***References***

1. Laudal, D.L. Evaluation of Alternatives to the Ontario Hydro Method as a Reference Method for CAMR. Final Report prepared AAD Document Control, U.S. Department of Energy, NETL, [www.netl.doe.gov/technologies/coalpower/ewr/mercury/control-tech/pubs/40321/40321-102Final%20Report.PDF](http://www.netl.doe.gov/technologies/coalpower/ewr/mercury/control-tech/pubs/40321/40321-102Final%20Report.PDF) (accessed Feb 2008).
2. Laumb, J.D.; Benson, S.A.; and Olson, E.A. X-Ray Photoelectron Spectroscopy Analysis of Mercury Sorbent Surface Chemistry. *Fuel Process. Technol.*, **2004**, 85 (6–7), 577–585.