

Evaluation of Sorbent Trap Materials and Methods for Flue Gas Mercury Measurement

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Technical Update, February 2009

EPRI Project Managers

C. Dene

N. Goodman

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This document was prepared by

URS Corporation 9400 Amberglen Blvd. Austin, TX 78729

Principal Investigators M. Richardson M. Owens K. Dombrowski

John T. Riley Consulting 1511 Woodhurst Street Bowling Green, KY 42104-3331

Principal Investigator J. T. Riley

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PRODUCT DESCRIPTION

Sorbent traps are used as an alternative to continuous mercury monitors (CMM) for measuring vapor phase mercury concentrations in stacks of coal-fired power plants and for relative accuracy test audits (RATAs) of CMMs. EPRI has an ongoing program of research on sorbent trap methods, evaluating the performance of sorbent materials and the methods used to measure mercury on the sorbent traps. This report presents results of two investigations targeted at evaluating the performance of sorbent trap methods for long-term monitoring and RATA testing.

Results and Findings

Sorbent traps have been used successfully to monitor mercury emissions from a large number of coal-fired power plant stacks. However, some testers have reported loss of mercury from the third section of the sorbent trap, which is spiked with a known amount of mercury prior to sampling as a quality control measure. Past EPRI research showed that this mercury spike can be lost over a period of days and that retention of mercury depends on the sorbent type and placement of the mercury on the third sorbent bed. The current investigation determined that sulfur dioxide levels in the flue gas affect the retention of mercury. The report makes recommendations for sorbent types and spiking configurations that may offer improved performance.

The EPA promulgated a sorbent trap reference method, EPA Method 30B, that can be used to conduct RATAs of continuous mercury monitors. Prior to analyzing RATA samples, a laboratory must complete several procedures designed to verify measurement accuracy. This report gives the results of tests and evaluations of Method 30B laboratory procedures conducted in two laboratories, using iodated and brominated sorbents.

Challenges and Objectives

Owners and environmental managers of U.S. coal-fired power plants who must monitor flue gas mercury emissions at their facilities need sampling and analysis methods that provide accurate data. EPRI's research provides information that can be used by facilities to evaluate sorbent trap monitoring systems and materials, as well as to obtain accurate analyses of the resulting samples.

Applications, Values, and Use

The results of EPRI's research will assist power plant monitoring staff and their laboratories in identifying factors contributing to success or failure in sorbent trap sampling and analysis.

EPRI Perspective

This report extends previous EPRI research, which included a round robin study of methods for sorbent trap mercury analysis and evaluation of mercury retention on sorbent traps.

Approach

Researchers passed synthetic flue gas simulating gases from a coal-fired power plant through pre-spiked sorbent traps and measured mercury loss both in the effluent gas and in the sorbent after sampling. To evaluate Method 30B, EPRI provided sorbent traps pre-spiked with mercury to volunteer laboratories.

Keywords Mercury Continuous mercury monitoring Sorbent trap

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1 INTRODUCTION

Background

Sorbent traps are used to measure mercury (Hg) in flue gas from combustion sources such as coal-fired power plants. Flue gas is pulled through a glass tube containing a sorbent material with an affinity for mercury. After sampling, the collected mercury is separated from the sorbent by heating, combustion of the sorbent, or solvent extraction, and measured by a mercury detector.

The U.S. Environmental Protection Agency (EPA) has accepted a sorbent trap method, referred to as "Appendix K", as an alternative to continuous mercury monitors (CMM) for measuring vapor phase mercury concentrations in stacks of coal-fired power plants. Recently, EPA also published Reference Method 30B, a sorbent trap method used for relative accuracy test audits (RATA) of mercury CMMs.

EPRI has conducted extensive research into sorbent trap mercury methods, beginning in the 1990s and continuing to the present, most recently:

- *Continuous Mercury Monitoring Guidelines*. 2007. 1012691- evaluated field applications of the sorbent trap method to RATAs.
- *Evaluation of Methods for Mercury Analysis of Appendix K Sorbent Traps.* 2007.1014565 reported results of a round robin laboratory study of four methods for measuring mercury in iodated, activated carbon sorbent traps.
- *Evaluation of Sorbent Materials for Flue Gas Mercury Measurement.* 2007. 1014046 compared the retention of mercury on iodated and brominated sorbents exposed to simulated flue gas. The report also evaluated the application of analytical techniques to measure mercury absorbed on brominated sorbent, and reported on a homogenation technique that can be used to subsample sorbent tubes for thermal or direct combustion analysis.

The current report summarizes work completed in 2008 to further investigate retention of mercury on Appendix K sorbent tubes, and also details a study of Method 30B laboratory procedures. Work on these issues is ongoing, and final results of these investigations will be reported in a future EPRI publication.

Report Organization

This report brings together results of two studies: 1) evaluation of the effect of SO_2 on retention of mercury by sorbent materials, and 2) evaluation of laboratory procedures in Method 30B. The experimental procedures and apparatus, results, and conclusions from the sorbent material study are contained in Sections 2-4, while the Method 30B evaluation is presented in Sections 5-8. References for both studies are presented in Section 9.

2 MERCURY RETENTION STUDY: EXPERIMENTAL DESIGN

Method Requirements

Appendix K is used for semi-continuous monitoring of stack mercury emissions. Typically, paired samples are collected over periods of days to a week. Appendix K was contained in the Clean Air Mercury Rule (CAMR), which was subsequently vacated by the D.C. Circuit Court; thus, it is not an official EPA method. However, the method is still referenced by some state's mercury regulations, and could potentially be included in future legislation.

Appendix K requires that each trap contain two beds of clean sorbent (typically an iodine- or bromine-treated activated carbon), followed by a third bed that has been pre-spiked with a known amount of mercury. The first bed is used to collect mercury from the flue gas, the second to detect breakthrough from the first bed, and the third to detect loss of mercury from the sorbent. Figure 2-1 illustrates the Appendix K tube configuration.



Figure 2-1 Sorbent Bed Configuration in an Appendix K Trap

Previous Research Findings

According to the Appendix K acceptance criteria, measurements are invalid if the mercury mass recovered from the third, spiked bed after sampling is completed falls outside $\pm 25\%$ of the true (spiked) value. Invalidation of an Appendix K sample is a concern for power plant operators, as the EPA's regulations require that missing or invalid sampling data must be substituted with conservative (high) assumed emission values.

In field demonstrations of the method, several sampling organizations observed instances of low recoveries of the third bed spikes. These anecdotal observations were confirmed by EPRI laboratory studies that observed desorption from pre-spiked beds exposed to simulated flue gas for 7 - 10 days [1]. It was determined that the placement of the spike on the sorbent bed had a major impact on the extent of loss from the trap. Placing the mercury spike on the front face of

the sorbent bed (the part first contacted by the flue gas) greatly improved mercury retention, but desorption still occurred from sorbent traps containing an iodated sorbent (Ohio Lumex). A test of a brominated sorbent (Sorbent Technologies) under identical conditions showed no loss of mercury.

Observations made during these laboratory studies suggested mercury desorption could be associated with the concentration of flue gas constituents, particularly sulfur dioxide (SO₂). This species was present in the EPRI simulated flue gas at 1000 ppm. In field studies using the same iodated sorbent (Ohio Lumex) where mercury loss was not observed, the SO₂ levels in the flue gas were lower (<500 ppm SO₂). This observation, as well as results from earlier EPRI test programs, indicates that SO₂ may reduce the adsorption and/or retention of mercury on carbon sorbents [1].

Design of Current Study

An additional round of laboratory testing was conducted to determine the concentration of SO_2 that might cause desorption of mercury from the pre-spiked beds. Tests were conducted in simulated flue gas containing SO_2 levels ranging from 200-1000 ppm SO_2 ; all other experimental parameters were held constant in each test. Iodated sorbents from Ohio Lumex, SKC, and Frontier Geosciences and a brominated sorbent from Sorbent Technologies were evaluated in this study. This report summarizes the results of the effect of SO_2 gas exposure tests.

Flue gas exposure tests were conducted at 200, 350, 500, and 1000 ppm of SO_2 . In these gas exposure tests, traps were exposed to approximately 400 mL/ min of simulated flue gas for seven days at 300°F. Catch solutions were placed downstream of each trap to catch any mercury that desorbed from the pre-spiked third bed. Each test was conducted at the same test parameters, only the SO_2 concentration was varied.

Table 2-1 summarizes the test matrix. The 1000 ppm test was the first in the series and included only traps containing Ohio Lumex iodated sorbent and Sorbent Technologies brominated sorbent. The results of the 1000 ppm test led to additional testing at lower levels of SO_2 and inclusion of the other sorbents. The number of replicates tested varied for each SO_2 concentration due to the addition of sorbents and a new spike configuration.

An additional parameter evaluated in this round of testing was the placement of the Hg spike on the pre-spiked bed. SKC offers Appendix K traps spiked using a vapor-phase, batch spiking process described below. Thus, two spike configurations were evaluated during two of the four gas exposure tests: 1) front-half spikes and 2) batch spikes. The batch spike was only evaluated on the SKC sorbent.

Front-Half Trap Spiking

All traps contained three one-gram beds of sorbent, separated by glass wool. The third bed of each trap was spiked in the front-half configuration with 40,000 ng of mercury. These traps were prepared by URS Corporation via the stannous chloride $(SnCl_2)$ dynamic spiking method, as described in an earlier report [1]. In a front-half spike configuration, a known mercury mass is loaded onto the front portion of the third sorbent bed. Figure 2-2 illustrates the location of the mercury on the third sorbent bed in an Appendix K trap spiked using a front-half configuration in relation to the direction of flue gas flow during testing.

Table 2-1 Impact of SO₂ on Mercury Desorption Test Matrix

			Bed 3 Pre-	No. of I	Replicates T	ested per C	ondition
Sorbent Vendor	Sorbent Type	Spike Placement	Spike Level ng Hg	200 ppm	350 ppm	500 ppm	1000 ppm
Sorbent Technologies	Brominated	Front Half	40,000	4	3*	3*	5
Ohio Lumex	Iodated	Front Half	40,000	4	3*	3*	5
Frontier Geosciences	Iodated	Front Half	40,000	4	3*	3*	not tested
SKC	Iodated	Front Half	40,000	4	3*	3*	not tested
SKC	Iodated	Batch Process	60,000	not tested	3*	3*	not tested

*Two replicates were evaluated for Hg desorption, the third replicate was evaluated for halogen desorption

Step 1: Spike the 3rd bed.

Hg Spike Flow



Step 2: Pack the other beds, expose to flue gas.



Flue Gas Flow



Batch spikes

The third bed of each batch-spiked trap was loaded with 60,000 ng of mercury using a vaporphase batch spiking methodology. These traps were prepared by SKC and provided to URS. SKC spikes batches of carbon sorbent with mercury-laden gas using a fluidized bed apparatus. When a batch of carbon is spiked using this approach, the mercury is adsorbed to the all carbon particles placed in the spiking apparatus. Figure 2-2 illustrates the location of the mercury on the third sorbent bed in an Appendix K trap containing carbon spiked using a batch methodology in relation to the direction of flue gas flow during testing.



Flue Gas Flow

Figure 2-3 Schematic of a Trap Containing Sorbent Spiked using a Batch Methodology

In a batch spiking process, it is assumed that the mercury adsorbs homogeneously to all carbon particles in the batch. The carbon batch is recovered at the end of the spiking process and subsamples are collected for mercury analysis. The results of the analyses are used to certify the spike concentration of the batch. The methodology SKC uses to spike batches of carbon is proprietary, so detailed information on their spiking procedure is not available.

Gas Exposure Tests

The simulated gas parameters were chosen to match those of flue gas found in a dry stack. A schematic of the system used to generate the simulated flue gas is shown in Figure 2-3. Gas settings and pressures were monitored daily to ensure the make-up of the simulated flue gas remained the same and within specifications to produce the expected gas component concentrations. Table 2-2 lists the components and concentrations of the simulated flue gas used in these tests. Colorimetric gas detection tubes (Dräger tubes) were used to spot check the SO₂ and NO_x concentrations before the start of each test. Measurements were within ±13% of the targeted SO₂ and NO_x concentrations.

Temperature Controlled Enclosure





Table 2-2Simulated Dry Stack Flue Gas for Effect of SO2 Tests

Flue Gas Component	Concentration (dry basis)
SO2	200, 350, 500, 1000 ppm
HCl	50 ppm
NOx	200 ppm
CO2	12%
O2	6%
H2O	6%
Hg	0 ppm

Figure 2-4 shows a diagram of the configuration of the test apparatus used to conduct the all SO₂ gas exposure tests. Simulated flue gas was generated and plumbed into a heated gas manifold composed of Teflon[®] fittings, tubing, and valves. The heated gas manifold was plumbed to deliver gas to 16 Appendix K traps that were placed in a temperature controlled oven. Approximately 400mL/min of simulated flue gas was pushed through each sorbent trap. The gas flow across the traps was controlled using a Teflon[®] valve placed upstream of each sorbent trap. The measured flow rates across the sorbent traps for all four tests ranged from 350 - 427 mL/min. The effluent gas exited the oven and bubbled into a glass catch bottle containing 10% ^v/_v hydrogen peroxide/ 5% ^v/_v nitric acid solution, then into a glass catch bottle containing 4% ^w/_v potassium permanganate/ 10% ^v/_v sulfuric acid solution. The catch solutions were configured analogous to a Method 29 train, and were meant to capture any mercury that desorbed from the pre-spiked sorbent bed.

Traps were exposed to flue gas at 300°F for seven days. The temperature of the oven and one trap effluent gas stream were monitored several times daily during each test. The trap effluent gas temperature was measured by a thermocouple installed in a Teflon[®] tee placed immediately downstream of the trap. The temperature of the trap effluent gas ranged from 293 - 305°F over the four tests. The average temperature of the trap effluent gas was 296°F.



Figure 2-5 Schematic of SO, Gas Exposure Test Apparatus

At the conclusion of each SO_2 exposure test, sorbent tubes were prepared for analysis using EPRI's modified version of the ASTM 6414 wet digestion method [1]. All sorbent traps and Method 29 catch solutions were analyzed on a flow injection mercury system equipped with cold vapor atomic fluorescence detection.

During the 350 and 500 ppm SO_2 tests, catch solutions designed to capture desorbed halogen species were placed downstream of one trap containing each sorbent type tested. The purpose of measuring desorbed halogen from the sorbent beds was to determine whether there is a correlation between halogen loss and mercury loss. Halogen catch solutions downstream of the iodated traps were composed of a carbonate buffer, and solutions downstream of the brominated trap were analogous to a Method 26 train (i.e., a sulfuric acid solution followed a sodium hydroxide solution).

3 MERCURY RETENTION STUDY: RESULTS

This section presents and discusses the results from the SO_2 gas exposure tests. In each gas exposure test, Appendix K traps were inserted in the test apparatus and exposed to flue gas at 300°F for seven days. Catch solutions configured similarly to a Method 29 train were placed downstream of each trap to catch any mercury that desorbed from the pre-spiked sorbent bed.

At the conclusion of each test, the pre-spiked sorbent bed and the Method 29 catch solutions were analyzed for mercury mass, and these analytical results were used to determine if desorption had occurred. A mercury mass balance was calculated for each trap/catch solution unit by dividing the sum of the mercury measured in the sorbent and catch solution by the theoretical mass of the pre-spiked mercury. In addition to the mass balance check, the percent recovery of pre-spiked mercury on the sorbent bed (i.e., bed 3) was calculated. Desorption was determined to have occurred when both of the following conditions were met:

- The percent of Hg recovered across the trap/solution unit was within the range of 80 120%
- Detectable amounts of mercury were measured in the Method 29 catch solutions.

Results that did not meet both criteria were considered suspect. The mass balance results showed that approximately one third (15 out of 46 trap/solution units tested) of the total mercury recoveries from trap/solution units fell outside of the acceptable range of 80-120% recovery. When these suspect data sets were further investigated, it was noted that the mercury recoveries on the pre-spiked mercury beds were very low (i.e., 53 - 79%), and there was no mercury detected in the Method 29 catch solutions. A table summarizing the mass balance recovery results is included in Appendix A. All potential causes of the low mercury recoveries were investigated, and notable findings are discussed in the paragraphs below.

The spiking and analytical processes were investigated by double checking the quality assurance/quality control (QA/QC) results and details of the preparatory steps. One of the most important QA/QC checks used to ensure the accuracy of the spiking and analytical processes is the analysis of a spiked trap called the "lot spike". A lot spike is retained from each batch of traps spiked, set aside (i.e., not exposed to flue gas), and analyzed for mercury with the tested traps. The mercury recovery results of all lot spikes fell within the accepted range of 85 -115%, thus ruling out problems with the spiking and analytical processes. Furthermore, all other analytical QA/QC results fell within accepted ranges.

The acceptable results for the lot spikes coupled with the low recoveries on the tested sorbent beds was puzzling. In the fifteen suspect data sets, 21 - 47% of the pre-spiked mercury was unaccounted for. To determine whether incomplete digestion of the sorbed mercury was responsible, a set of digested sample beds was digested a second time. Very little mercury was found in these digestates. The missing mercury was never located, and the cause of the poor recoveries is unknown. However, it is speculated that the problem is related to the ability of the acid digestion matrix to quantitatively recover mercury from traps with high mercury loadings that have been exposed to flue gas.

Due to the experimental problems discussed above, desorption was calculated using only the mercury measured in the Method 29 catch solutions. The Method 29 results were considered reliable based on the results of two types of matrix spikes. One matrix spike was inserted in the test apparatus (i.e., spiked catch solutions were exposed to flue gas), and the second type of matrix spike was prepared fresh (without gas exposure) and digested with each analytical batch of catch solution samples. The recovery results of these matrix spikes fell within the acceptable range of 90 - 110% of the theoretical value.

Table 3-1 summarizes the desorption data for all SO_2 gas exposure tests; the detailed results are tabulated in Appendix B. The amount of Hg that desorbed from each pre-spiked sorbent bed is expressed as a percent Hg loss, which was calculated by dividing the mass of mercury measured in the Method 29 catch solutions by the theoretical mass of pre-spiked mercury. The results of all replicates are presented in Table 3-1. An entry of "no loss" indicates the mercury measurement in the combined Method 29 impingers was below the detection limit of approximately 900 ng Hg, meaning there was less than a 2% loss of mercury from the pre-spiked mercury bed.

			Percent Hg Loss, Based on Hg in M29 Catch Solutions			
Sorbent Vendor	Sorbent Type	Spike Configuration	SO ₂ = 200 ppm	SO₂ = 350 ppm	SO ₂ = 500 ppm	SO ₂ = 1000 ppm
Sorbent Technologies	Brominated	Front-half	no loss**	no loss**	no loss**	no loss**
Ohio Lumex	Iodated	Front-half	no loss**	no loss**	no loss**	4, 19, 21, 36, 50%
Frontier Geosciences	Iodated	Front-half	no loss**	no loss**	no loss**	NT*
SKC	Iodated	Front-half	no loss**	no loss**	no loss**	NT*
SKC	Iodated	Batch	no loss**	11, 14%	18 ,31%	NT*

 Table 3-1

 Summary of Percent Hg Loss for All SO₂ Gas Exposure Tests

*NT = not tested

**no loss = Hg measurement of M29 catch solutions was below detection limit of approximately 900 ng Hg

The following observations were made regarding the results from all SO₂ gas exposure tests:

- Sorbent Technologies brominated sorbent did not lose mercury from the pre-spiked third bed with any of the SO₂ concentrations tested.
- No iodated sorbents spiked in the front-half configuration lost mercury in the 200, 350, and 500-ppm SO₂ tests.
- The Ohio Lumex sorbent was the only iodated sorbent tested at 1000 ppm. This sorbent had losses ranging from 4 50% of the spiked Hg.
- The SKC batch-spiked sorbent lost mercury in the 350 and 500 ppm SO₂ tests, while the SKC front-half spiked traps did not show any losses in those tests. The losses from the SKC batch-spiked traps increased with increasing SO₂ concentration.

• Losses varied among replicate traps. For example, the five Ohio Lumex traps tested at 1000 ppm SO, had losses ranging from 4 - 50%.

In an actual compliance monitoring scenario, mercury measurement data obtained from an Appendix K trap are considered valid only if the post test recovery of the pre-spiked Hg falls within $\pm 25\%$ of the theoretical value spiked (i.e. losses cannot exceed 25% during exposure to flue gas). Although losses were measured in this study, a large majority of the traps would have met the Appendix K criteria and been considered reportable data. For example, only one of the four SKC batch spiked traps that experienced measurable losses at 350 - 500 ppm SO₂ would have failed to meet the Appendix K criteria, while only two of the five Ohio Lumex traps that experienced measurable losses at 1000 ppm would have failed.

During the 350 and 500 ppm SO₂ tests, catch solutions designed to capture desorbed halogen species were placed downstream of one trap containing each sorbent type tested. The purpose of desorbed halogen measurement was to attempt to evaluate a correlation between halogen loss and mercury loss. Table 3-2 summarizes the concentrations of iodide and bromide measured in the catch solutions. The levels observed ranged from 32 - 109 ppm for iodated sorbent and from 74 - 85 ppm for brominated sorbent. The amount of halogens captured did not appear to increase with increasing SO₂ concentration.

To ascertain whether halogen loss is associated with sorbent tube failure (either by removing adsorption capacity for mercury or carrying mercury out of the tube) a percent halogen loss would need to be calculated; however the starting concentrations of halogen on each sorbent are unknown considered proprietary by the vendors.

			Halogen (ppm) Measured in Catch Solution			
Sorbent Vendor	Sorbent Type	Spike Configuration	SO ₂ = 200 ppm	SO ₂ = 350 ppm	SO ₂ = 500 ppm	SO ₂ = 1000 ppm
Sorbent Technologies	Brominated	Front Half	NM	74	85	NM
Ohio Lumex	Iodated	Front Half	NM	91	109	NM
Frontier Geosciences	Iodated	Front Half	NM	33	39	NM
SKC	Iodated	Front Half	NM	40	51	NM
SKC	Iodated	Batch Process	NM	32	30	NM

Table 3-2Summary of Halogen Measured in the Catch Solutions

*NM = not measured

4 MERCURY RETENTION STUDY: CONCLUSIONS

Summary and Conclusions

Tests were conducted to evaluate the effect of SO_2 on the retention of mercury on the pre-spiked third bed of an Appendix K trap. Traps were exposed to simulated flue gas containing SO_2 levels ranging from 200-1000 ppm, for seven days at 300°F. Sorbents from four vendors (Ohio Lumex, SKC, Frontier Geosciences, Sorbent Technologies) were evaluated, including both iodated and brominated sorbents and front-half and batch-spiked configurations. For each test, the amount of Hg that desorbed from each pre-spiked sorbent bed was determined by measuring Hg in Method 29 catch solutions.

The data showed that SO_2 can have a negative impact on the retention of mercury on the prespiked beds. For the traps that experienced Hg loss, the amount of desorption increased with increasing SO_2 concentration in the flue gas.

For traps spiked in the front-half configuration, none of the four sorbents tested showed any loss of mercury at SO₂ concentrations at or below 500 ppm. Only two sorbents (Ohio Lumex and Sorbent Technologies) were tested with 1000 ppm SO₂. Losses were observed with the Ohio Lumex iodated sorbent, while no measurable loss was observed with the Sorbent Technologies brominated sorbent. Thus, the brominated sorbent may be a better choice for long term (i.e., seven days) mercury measurement in gases containing levels of SO₂ greater than 500 ppm. As only one iodated sorbent was tested with1000 ppm SO₂, it is not known if all iodated sorbents will lose mercury at elevated SO₂ concentrations.

Spike placement is an important determinant of mercury loss from the pre-spiked sorbent bed. A comparison of mercury loss from front-half spiked and batch spiked beds of the same SKC sorbent show that the batch spiked beds lost mercury when exposed to 350 and 500 ppm SO₂, while the front-half spiked beds showed no measurable loss at these SO₂ levels. These data, coupled with the results of earlier spike optimization studies, show that placement of the mercury on the front portion of the sorbent bed will increase the likelihood of meeting the Appendix K recovery criteria [1]. Even front-half spiked traps may experience mercury desorption at higher SO₂ concentrations. Shortening the flue gas exposure time may mitigate these losses, and success with this strategy has been reported by some utilities.

The desorption results show that all four sorbents can retain mercury on a front-half spiked sorbent bed when exposed to a dry stack flue gas containing 500 ppm or less of SO_2 for seven days. These results are promising for future implementation of the sorbent tube method, as the implementation of the Clean Air Interstate Rule (CAIR) will require most power plants to lower stack SO_2 levels to well under 500 ppm SO_2 .

Future Work

Future testing will evaluate the effect of sulfur trioxide (SO_3) on both adsorption and desorption of mercury in Appendix K traps. SO₃ is formed from SO₂ oxidation in the furnace and across a

SCR. The presence of SO₃ in flue gas has been observed to adversely affect Hg adsorption to activated carbon injected into boilers for mercury treatment. Laboratory testing efforts have begun, but experimental problems have been encountered in generating a reproducible concentration of SO₃ in the synthetic flue gas. Results from the effect of SO₃ tests will be reported in a future technical update.

5 EVALUATION OF METHOD 30B LABORATORY PROCEDURES

Introduction

EPA Method 30B is a Reference Method used to conduct relative accuracy test audits (RATAs) of continuous mercury monitors (CMMs) or sorbent trap (Appendix K) sampling systems installed at coal-fired electricity generating units. The method uses glass tubes packed with a sorbent material to trap mercury from the flue gas. The mercury in the sorbent traps is measured either by chemical extraction and analysis or by a thermal analytical technique. This method is intended for use only under relatively low particulate conditions (i.e., sampling after all pollution control devices). The method is designed to measure the mass concentration of total vapor phase Hg in flue gas. Vapor phase Hg includes elemental (Hg⁰) and oxidized forms (Hg²⁺).

Method 30B was promulgated by the EPA as an amendment to the Clean Air Mercury Rule (CAMR) on January 4, 2008. The final method is included in 40CFR Part 60, Appendix A-8 and is available online [2]. The CAMR was vacated by the D.C. Circuit Court in February, 2008, removing the requirement for mercury monitoring at many facilities. However, states that adopted their own mercury control regulations are requiring power plants to adhere to the federal monitoring regulations.

Most power plants operating CMMs or Appendix K samplers for regulatory reporting are using Method 30B for RATAs, in preference to three other permissible alternatives: EPA Method 30A, Ontario Hydro, and EPA Method 29. EPA's instrumental reference method 30A, published at the same time as 30B, is still under development. The Ontario Hydro Method and EPA Method 29 are used less frequently due to greater complexity and slower turnaround time than Method 30B. The Hg sorbent trap approach is less onerous to use than either Ontario Hydro or Method 29, and although it does not measure real-time Hg concentrations, a thermal technique can be used to analyze the samples on the same day that they are collected.

Method 30B is a performance-based method, in that the sorbent material and mercury measurement technique are not specified in the method. The method contains performance specifications that must be met for a measurement to be acceptable for a RATA. The method also specifies procedures that must be followed to ensure measurement quality; these include tests that must be completed by the tester prior to analyzing any samples, quality control measurements for each RATA sample, and procedures for calibrating and determining the sensitivity of analytical instruments.

Method 30B has not been thoroughly tested to determine whether the method specifications and procedures are realistic and practical. EPRI has conducted research on other sorbent trap method applications, including a study of the analytical procedures used in Appendix K monitoring [3]. That study evaluated method performance with several sorbents and a range of mercury loadings,

including less than 100 ng mercury per trap, a loading anticipated for many Method 30B analyses.

EPRI conducted this study to evaluate the practicality and statistical robustness of the laboratory procedures specified in Method 30B. The results of the study will be used to provide input to EPA on future revisions of Method 30B, and to provide guidance to EPRI members on application of the method.

Method 30 B Laboratory Requirements

The EPA Method 30B Quality Assurance and Quality Control (QA/QC) performance criteria for mercury measurements, whether conducted using an on-site instrument or in a laboratory, are summarized in Table 5-1. Additional QC criteria apply to field sampling (e.g., calibration of flow monitors) but those are not addressed in this study.

Method 30B specifies several procedures that laboratories must complete before they can analyze RATA samples. Some of these are done once, while others must be completed for each combination of a sorbent material and an analytical method. The primary objectives of these performance tests are to verify the performance of the analytical system and to identify the minimum amount of Hg that must be collected on the sorbent trap to give accurate quantification. Each laboratory is required to measure the following parameters.

Method Detection Limit – The Method Detection Limit (MDL) is the lowest mass of Hg greater than zero that can be estimated and reported by the candidate analytical technique. An MDL shall be determined for each analytical instrument, sorbent, and sample size to be used in the study. Method 30B states that an MDL is calculated "using an MDL study such as that found in section 17.0 of the proposed amendments to EPA Method 301 (69 FR 76642, 12/22/2004)". By this procedure, the MDL is equal to three times the standard deviation of the measured Hg concentration in an unspiked (blank) sample, based on seven or more replicate analyses. However, EPA has not precluded the use of other statistical methods for determining the detection limit.

Determination of Minimum Calibration Concentration or Mass – This procedure is used to determine the smallest amount of Hg that can be measured accurately in a field sample with a specific analytical method. The MCC/MCM should be higher than the lowest instrument calibration point, so that analytical variability will not cause field measurements to fall outside the calibration range. Depending on the analytical method and type of calibration standard used (liquid or solid), this parameter may be expressed as a concentration (µg Hg per liter of digestate) or as a mass (e.g., ng Hg per sorbent sample).

Table 5-1Method 30B QA/QC Requirements for Laboratories

QA/QC Test or Specification	Acceptance Criteria	Frequency	Consequences if Not Met
Analytical matrix interference test (only for wet chemical analysis)	Establish minimum dilution needed to eliminate sorbent matrix interferences. Measured Hg ± 5% of a solution without digestate.	Once per laboratory, prior to analyzing any field samples; repeat for each type of sorbent used	Field sample results not validated
Minimum sample mass	Establish minimum mass of Hg per sample needed for quantification. No acceptance criterion.	Once per laboratory, for each analytical method, sample size, and sorbent material, prior to analyzing field samples	Field sample results not validated
Analytical bias test	Average recovery between 90% and 110% for Hg° and HgCl ₂ at each of two spike concentration levels	Once per laboratory, for each analytical method and sorbent material, prior to analyzing field samples	Field samples shall not be analyzed until the percent recovery criterion has been met
Multipoint analyzer calibration	Each analyzer reading within \pm 10% of true value and $r^2 \ge 0.99$	On the day of analysis, before analyzing any samples	Recalibrate until successful
Analysis of independent calibration standard	Within ± 10% of true value	Following daily calibration, prior to analyzing field samples	Recalibrate and repeat independent standard analysis until successful
Analysis of continuing calibration verification standard (CCVS)	Within ± 10% of true value	Following daily calibration, after analyzing ≤ 10 field samples, and at end of each set of analyses	Recalibrate and repeat independent standard analysis, reanalyze samples until successful, if possible: for destructive techniques, samples invalidated

The first step in determining the MCC/MCM is to establish a single, low-level, calibration curve for each instrument, taking into account the instrument's sensitivity and linearity range. The lowest point in the calibration curve should be at least 5 and preferably 10 times the MDL of the instrument. Second, a mercury concentration or mass is identified within that calibration range, for a particular sample dilution and/or sample size. The method specifies that the MCC/MCM should be at least two times the lowest point in the calibration curve. Examples of MCC and MCM determinations are shown in 5- 1 and 5-2, for thermal and acid digestion methods, respectively.

Determination of Minimum Sample Mass (MSM) – The minimum mass of Hg that needs to be collected per sample must be determined for each method, instrument, and sample dilution.

The minimum sample mass for the Thermal Desorption (TD) and Direct Combustion Analysis (DCA) methods is the same as the minimum calibration mass (MCM), because there is no dilution – the entire sample is used in the analysis. The equation for the calculation of the minimum sample mass for sorbent extracts (wet chemical analysis) is as follows:

MSM = MCC (ng/L) * final digestate volume (L) * dilution factor (DF)

Calculations of MSM for thermal and acid digestion methods are shown in Figures 5-1 and 5-2, respectively.

Each laboratory needs to consider the Hg background (sorbent blank concentration) in selecting the minimum sample mass, so that samples do not frequently fail the criteria for Section 2 breakthrough:

Section 2 mass <10% of Section 1 Hg mass, for Hg emissions > 1 μ g/dscm

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Section 2 mass <20% of Section 1 Hg mass, for Hg emissions \leq 1 µg/dscm
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For example, if a minimum sample mass of 20 ng was selected for a stack with emissions above $1 \mu g/dscm$, a second section Hg mass above 2 ng would invalidate the sample. If a laboratory knows that their method blanks are averaging 5 ng, they would need to select a MSM of at least 50 ng to avoid having test runs invalidated.



Figure 5-1 Example Determination of MCM and MSM for Thermal Desorption Analysis


Figure 5-2 Example Determination of MCC and MSM for Wet Digestion Analysis

Method 30B Sampling and Analytical Methods

This study focused on laboratory procedures required by Method 30B; field procedures were not evaluated. However, a general description of the sorbent trap field procedures is provided here.

Sampling Procedures

A sample of flue gas is continuously drawn through two glass tubes arranged in parallel. Each trap contains two beds of activated carbon or another sorbent material in series, separated by quartz wool plugs. The first bed contacted by the flue gas is used to measure the mercury content of the flue gas and the second is used to determine breakthrough. After sampling, the trap ends are sealed. The Hg captured by the sorbent is then either thermally desorbed into a mercury detector or the tubes are transferred to a laboratory for extraction of Hg and analysis.

For a RATA of an appendix K monitoring system, the sorbent material used in the appendix K sorbent traps must be the same as that used for daily operation of the Appendix K monitoring system. However, traps used for RATA testing can be smaller than the traps used for daily Appendix K monitoring. The smaller traps are particularly advantageous at very low Hg concentrations, as the smaller mass of sorbent gives better sensitivity and facilitates shorter RATA test run times.

Method 30B requires a field recovery test to be performed for each RATA. The test must include three paired runs of which one trap in each pair is spiked with Hg at a level between 50 - 150% of the expected trap loading, as calculated from the expected flue gas concentration and gas flow rate.

Sorbents used in Method 30B and Appendix K testing are typically activated carbon that has been chemically treated to better retain mercury. Both iodine and bromine-treated sorbents have been shown to be effective in previous testing, although losses of mercury spikes have been observed in the laboratory with long gas exposures and in the presence of high levels of sulfur dioxide [1]. Loss of mercury spike is unlikely to be a problem for Method 30B tests, which are typically short-term (a few hours in duration).

Analytical Procedures

Method 30B, as a performance-based method, does not specify the methods to be used to recover the trapped mercury from the sorbent and to measure the trap loading. The method lists recovery techniques that may be appropriate, including acid leaching, digestion, and thermal desorption/ direct combustion. Measurement techniques that may be appropriate include but are not limited to atomic fluorescence spectroscopy (AFS), atomic absorption spectroscopy (AAS) with and without gold trapping, and X-ray fluorescence (XRF) analysis.

6 METHOD 30B STUDY: EXPERIMENTAL DESIGN

Two power company laboratories participated in the study:

- American Electric Power's Dolan Laboratory
- Tennessee Valley Authority (TVA) Muscle Shoals Laboratory

Sorbent traps used in this study were small, Method 30B traps, each containing two beds (0.15 g to 0.2 g each) of iodated or brominated sorbent. Iodated sorbent tubes and bulk sorbent were obtained from Ohio Lumex Company (9263 Ravenna Rd., Twinsburg, OH) and brominated sorbent tubes and bulk sorbent were obtained from Sorbent Technologies Corporation (1664 E. Highland Rd., Twinsburg, OH).

URS Corporation's laboratory in Morrisville, NC prepared the spiked traps and confirmed the spiking levels by analyzing a set of traps using the thermal desorption method.

Laboratories were instructed to follow the procedures in Draft EPA Method 30B. Each laboratory was provided with a set of project materials for each analytical method used:

- Three sets of 10 iodide-treated sorbent tubes spiked at three levels between 20 and 100 ng for the Hg⁰ bias test.
- Three sets of 10 bromide-treated sorbent tubes spiked at three levels between 20 and 100 ng for the Hg⁰ bias test.
- Bulk sorbents, both iodide-treated and bromide-treated

For the Hg⁰ analytical bias test, each laboratory was provided with 10 sorbent tubes spiked at each of three levels between 20 and 100 ng (30 tubes), for each sorbent and each analysis method. The 10 replicates per level are more than is required by Method 30B, but were provided to allow for better statistical evaluation.

For the HgCl₂ analytical bias test, each lab was asked to prepare 10 replicate spikes at each of three levels between 20 and 100 ng Hg²⁺, for each sorbent and analytical method. Originally, EPRI provided spiking solution; however, it was determined that the Hg level in these solutions had degraded during transport. Therefore, the participants used fresh lots of their own commercial stock solutions to prepare the spikes. Different microliter volumes of 1 ng/µl and ~10 ng/µl HgCl₂ solutions were added to about 0.15 g portions of sorbent to prepare 10 replicates at three levels, between 20 and 100 ng Hg²⁺, for each sorbent.

Each laboratory was requested to report data and calculations for each of the following parameters:

- Method Detection Limit (MDL)
- Analytical Matrix Interference Test
- Analytical System Calibration

- Minimum Calibration Concentration or Mass
- Minimum Sample Mass
- Hg⁰ Analytical Bias Test
- HgCl, Analytical Bias Test
- Target Sample Volume

Analytical methods used in the current study are summarized below. Detailed procedures for these methods have been published previously (EPRI, 2007a; EPRI, 2007b).

Draft EPA Method 324 – Acid Extraction/AFS or AAS (324) - EPA published *Draft Method 324 – Determination of Vapor Phase Flue Gas Mercury Emissions from Stationary Sources Using Dry Sorbent Trap Sampling – Subsection: Analysis Method by CVAFS in the proposed CAMR (68 FR 4652, January 30, 2004), but did not include a detailed method in Appendix K of the final Rule. In Draft Method 324, the solid sorbent material is extracted in a hot, 70:30 ratio mixture of concentrated nitric/sulfuric acid, the solution is filtered, and the extract is diluted with bromine chloride (BrCl, also referred to as bromine monochloride). Elemental mercury released from the analyte solution through reduction is pre-concentrated on a gold amalgamator and analyzed using a cold vapor AFS instrument. The method, as originally developed by Frontier Geosciences, was validated for AFS only, but use of AAS is also allowed. High dilutions of the extract solution (100 times or more) are used to minimize chemical interference.*

Thermal Desorption/AAS (TD) - In this method, the solid sorbent material is placed in a ladle, which is loaded into an Ohio Lumex RP-M324 Thermal Decomposition Furnace attached to an RA-915 Mercury Analyzer. The sample is heated in air, which ignites carbon-based material and generates carbon monoxide (CO), an excellent reducing agent. The heated sample and CO release elemental mercury from the sample, which is determined by AAS with Zeeman correction. The signal is integrated over time, giving a measure of the total mercury evolved from the sample during the analysis. The instrument must be calibrated with the same type of material that is being analyzed. In this study, a NIST traceable mercury solution spiked onto a halogen-treated activated carbon was used as the calibrant when analyzing samples.

In this study, the flow through the analyzer was set at 2 liters/min to optimize the sensitivity of the instrument. (This is lower than the factory default setting of 4 liters/min used in previous studies). The system was further optimized for low level measurements by increasing the temperature of the analyzer furnace to above 620°C. The high temperature of the furnace quickly evolves the mercury off the carbon to yield sharp, consistently shaped peaks.

Modified ASTM D 6722 – Direct Combustion/AAS (DCA) - This method uses the analytical procedures in ASTM Standard D 6722 – Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis and Atomic Absorption Spectroscopy [4]. A sample of solid sorbent material weighing up to 0.25 g is placed into a nickel boat and analyzed with a LECO AMA 254 Mercury Analyzer. The weighed sample is dried at 100-120°C and combusted at 750°C in oxygen. The combustion gases pass over a catalyst heated at 750°C, which scavenges acid gases and condensable materials, and then over an amalgamator which captures mercury. Heating the amalgamator to 900°C releases the captured mercury into the vapor phase for quantitative analysis by AAS. The instrument is calibrated with solid NIST standard reference materials. A procedure for homogenation of sorbent materials that allows subsampling and multiple runs on sorbent materials from Appendix

K tubes was developed in a previous EPRI study [1]. This procedure was developed primarily for use with ASTM Standard D 6722.

7 METHOD 30B STUDY: RESULTS AND DISCUSSION

Method Detection Limit

Analytical data were submitted for three methods: Draft EPA Method 324 (324), Thermal Desorption (TD), and Direct Combustion Analysis (DCA). Table 7-1 lists the MDLs for the three analytical methods and the two sorbent materials. The Method 324 values were calculated using the values determined for the 10 section-2 or "B" sides of the 20-ng spiked sorbent tubes. The analyses used all the bed material (0.15 - 0.2 g) in these tubes. Assuming there was no Hg breakthrough into the second section of the tubes, this material served as a true method blank for the analyses. The very low average Hg in the second sections (all < 1 ng Hg) is a good indication there was no Hg breakthrough. The MDL values for the DCA and TD methods were calculated using seven to eight runs for each sorbent.

	lodated Sorbent			Brominated Sorbent		
Method	324	DCA	TD	324	DCA	TD
Blank average, ng	0.63	0.18	-0.07	0.89	0.17	0.07
Standard deviation of blanks	0.26	0.026	0.24	0.19	0.084	0.52
Method Detection Limit (MDL), ng	0.78	0.079	0.73	0.58	0.25	1.55

Table 7-1 Method Detection Limits for Mercury in lodated and Brominated Sorbents

Analytical Matrix Interference Test

Analytical matrix tests were performed by one laboratory using Draft Method 324. The results of this determination for iodated and brominated sorbent are shown in Figure 7-1. For iodated sorbent, the recovery of mercury increased smoothly with dilution factor. A minimum extract dilution of 20 brought the interference to an acceptable level (< 5%). For brominated sorbent, the observed analytical matrix interference was smaller, and the recovery first increased from dilutions of 2 to 25, then decreased. The laboratory selected a dilution of 5, which had a percent recovery above the acceptable range (107.2%). Inspecting the recovery curve, acceptable recoveries were obtained with dilution factors of 2 and above 25. It would have been advisable for the laboratory to perform an additional investigation of the source of the high bias for this sorbent. Data collected in these determinations is given in Appendix A.



Figure 7-1 Analytical Matrix Interference Test for Draft Method 324

Analytical System Calibration

Multipoint calibrations of each of the mercury analysis systems used in this study were performed before each of the bias tests. The calibration data met the acceptance criteria outlined in Table 7-1. The calibration concentrations and average correlation (r^2) values for each method are summarized in Table 7-2. During the course of the study the analysts ran check samples after 10 runs and the end of each analysis. The values of the check samples were within ± 10 percent of the true values.

Table 7-2Multipoint Calibration Results

Method	Calibration Standards (ng)	Average r ²
Draft Method 324	1, 5, 10, 25, 100	0.9995
TD – lodated sorbent ¹	10, 20, 40, 60, 80, 100	0.9999
TD – Brominated sorbent ¹	10, 20, 40, 60, 80, 100	0.9999
DCA – lodated sorbent ²	1.4, 3.5. 7.0, 14, 21	0.9996
DCA – Brominated sorbent ²	1.4, 3.5. 7.0, 14, 21	0.9989

¹TD method was calibrated with bulk sorbent material

²¹DCA method was calibrated with a NIST coal standard, 1633b

Minimum Sample Mass

As discussed above, the minimum sample mass (MSM) is determined by the minimum calibration concentration or minimum calibration mass (MCC/MCM), which should be at least twice the lowest point in the calibration curve. Table 7-3 indicates the lowest calibration point, the MCM/MCC selected for each method and sorbent, and the MSM calculated from the MCM/MCC values.

	lod	ated Sorb	pent	Brom	inated So	orbent
Method	324	DCA	TD	324	DCA	TD
	0.78	0.079	0.73	0.58	0.25	1.55
	1.0 ¹	1.4	10	1.0 ¹	1.5	10
		2.8	20		3	20
	10			10		
		2.8	20		3	20
	20			5		
	10			2.5		
	Method	Ioda Method 324 0.78 1.01 10 20 10 10	Iodated Sort Method 324 DCA 0.78 0.079 1.0 ¹ 1.4 2.8 2.8 10 2.8 20 10 10 10	Iodated Sorbent Method 324 DCA TD 0.78 0.079 0.73 1.01 1.4 10 2.8 20 10 2.8 20 20 2.8 20 10 2.8 20 10 10 10	Iodated Sorbent Brom Method 324 DCA TD 324 0.78 0.079 0.73 0.58 1.0^1 1.4 10 1.0^1 2.8 20 10 10 2.8 20 5 5 10 2.5 2.5 2.5	Iodated Sorbent Brominated Sorbent Method 324 DCA TD 324 DCA 0.78 0.079 0.73 0.58 0.25 1.0^1 1.4 10 1.0^1 1.5 2.8 20 3 10 2.8 20 3 20 2.8 20 3 20 5 10 2.5

Table 7-3Calculation of Minimum Sample Mass (MSM)

¹ Lowest calibration point did not meet method criterion of at least 5 times MDL.

 2 V = total volume of digestate (0.05 L); DF = dilution factor.

The calculated minimum sample masses for the three methods ranged from 2.8 to 20 ng Hg for iodated sorbent, and from 2.5 to 20 ng for brominated sorbent. This study shows DCA yielded the lowest minimum sample mass values for both sorbents. Low levels were obtainable by all three methods, indicating they are all viable for RATA and emissions testing. These values indicate that all three methods, performed carefully by skilled laboratory personnel, can achieve good success at mercury concentration levels well below those reported in previous studies.

The lowest calibration point used for the Draft Method 324 analyses was less than 5 times the MDL calculated from sorbent blanks, measured at the minimum dilution determined in the analytical bias tests. However, the MDL for a Hg standard in water on this particular instrument is 0.1 ng/L, or 0.005 ng Hg for a 50-ml volume of sample. Therefore, it is questionable which approach should be used to determine the MDL. Use of the lower MDL would produce unrealistically low MSM values, but sorbent blanks contain enough Hg that they may produce MSM values much higher than can be quantified accurately.

Section B Breakthrough - Each laboratory needs to consider the Hg background (sorbent blank concentration) in selecting the minimum sample mass, so that samples do not frequently fail the criterion for Section B breakthrough:

Section 2 mass <10% of Section 1 Hg mass for Hg emissions > 1 μ g/dscm

Section 2 mass <20% of Section 1 Hg mass for Hg emissions \leq 1 µg/dscm

The average masses of mercury determined for the back sections (Section B) in the sorbent tubes spiked with Hg^0 are given in Table 7-4, along with the minimum sample mass (MSM) values and 10% and 20% of the MSM values. The MSM values for the 324 and TD methods are high

enough that background Hg levels should not be a concern relative to a MSM loading. However, using the DCA method, an iodated sorbent trap with a Hg loading equal to the MSM would fail the background criterion often, as two of the three spike levels had average blanks equal to or higher than 10% and 20% MSM. All of the brominated spike levels had average blanks greater than 10% and 20% MSM.

	lod	Iodated Sorbent			Brominated Sorbent		
Method	324	DCA	TD		324	DCA	TD
	Average Section 2 Hg (ng)						
20.9 ng Hg° Spike	0.63	0.12	0.40		0.89	0.46	0.47
41.3 ng Hg° Spike	0.59	0.27	0.52		1.08	0.63	0.69
80.3 ng Hg° Spike	0.72	0.61	0.26		0.85	1.13	0.45
	Mi	nimum Sa	mple Mas	s (ng Hg)		
MSM	10	2.8	20		2.5	3	20
10% of MSM	1.0	0.28	2.0		0.25	0.3	2.0
20% of MSM	2.0	0.56	4.0		0.50	0.6	4.0

Table 7-4 Comparison of MSM with Allowable Section B Breakthrough

This evaluation suggests that the MSM for the DCA method needs to be increased to avoid the risk of having RATA runs invalidated by the breakthrough criterion.

Practical Quantitation Limit

An additional term to consider for this study, although not required by Method 30B, is the *Practical Limit of Quantitation* (PLQ). The PLQ is the lowest level above which quantitative results may be obtained with an acceptable degree of confidence [5]. A calculated limit of quantitation (LOQ) is defined as 10 times the standard deviation of a series of at least 7 blank runs. The calculated LOQ corresponds to an uncertainty of ± 30 percent at the 99% confidence level. For many applications the calculated LOQ is used to establish the lower limit of a test method. The practical limit of quantitation (PLQ) is then estimated by choosing a calibration mass or concentration above the calculated LOQ, preparing the calibrants, and running at least 7 runs. The standard deviation of the chosen calibrant. If the PLQ is more than 2 times the calculated LOQ, a better estimate of the PLQ is made by preparing three calibrants, running the three series, and plotting the standard deviations versus the mass or concentration of the claibrant at zero mass or concentration of the linear plot and multiplied by 10 to yield the PLQ.

For the Direct Combustion Analysis (DCA) method the calibration data submitted with the laboratory set is sufficient to estimate a Practical Limit of Quantitation (PLQ). The lowest points in the calibration curve, as listed in Table 7-3, were determined using three runs of NIST standard 1633b at each calibration point. The standard deviations of the runs at the lowest calibration mass values were 0.03 for the iodated sorbent calibration and 0.04 for the brominated sorbent calibration. Multiplying each of these values by 10 gives estimated PLQs of 0.3 ng and 0.4 ng for the DCA procedure. These values are well below the lowest calibration mass (1.4 and

1.5 ng). Consequently, the minimum sample mass values reported for the determination of mercury in lab samples are well above the potential lowest limits of the instrument used in this particular method.

Hg^o Analytical Bias Test

Each laboratory was provided with 10 sorbent tubes spiked at three levels between 20 and 100 ng for each sorbent and each analysis method. These samples were used in the Hg⁰ analytical bias test. A set of data was submitted for each of the three analytical methods, along with a set of thermal desorption data from the URS Corporation. The latter data was for the confirmation of the spiking levels in the sorbent tubes.

Figure 7-2 shows the averages (n = 10) reported for the mercury in the spiked iodated sorbent tubes, determined by the three different methods. Averages for all four sets of data ranged between 96 and 109% recovery for Method 30B tubes. All recoveries were within 90 to 110%, the specified acceptance criteria for this test. The level of performance in this study is much better than that in a previous study, which included sample tubes spiked at the 40 ng level (2).

Figure 7-3 shows the averages reported for the mercury in the spiked brominated sorbent tubes, determined by the three different methods. Averages for all four sets of data ranged between 85 and 118% recovery. The two sets of results reported for the Thermal Desorption (TD) method were within the 90 to 110% acceptance criteria. The results for Draft EPA Method 324 (324) recoveries were all higher than the 110% upper acceptance criterion. Two of the three results for the direct combustion analysis (DCA) method were below the 90% acceptance criterion. Some observations and results reported by the analysts for the 324 and DCA methods have some bearing on these results.

In the analysis of the spiked brominated sorbent tubes by Draft Method 324, the analytical matrix interference test showed an increase in the analytical signal with an increase in dilution factor. As shown in Figure 7-1, this increase peaked at a dilution of 10 (109%) and did not decrease to 100% until the dilution was near 50. If the analyst had used the analytical response at a dilution of 2 (103.5%) instead of the analytical response at a dilution of 5 (107.2%), the percent recoveries in the analytical bias test would likely have been 103.5/107.2 times those reported. Only the 41.3 ng sample would have exceeded the 110% acceptance level. Using a dilution of 50, all three spike levels would have been acceptable. The cause of the positive analytical signal interference(s) in the extracts from the brominated sorbent are unknown and, in the future, further evaluation of matrix interferences would be recommended prior to running the analytical bias tests.

In the analysis of the spiked brominated sorbent tubes by the direct combustion method (DCA), the lab analysts reported that the catalyst in the LECO AMA 254 Mercury Analyzer appeared to deteriorate toward the end of the analyses. This may explain the poorer recovery of the mercury in the brominated sorbent tubes. The iodated samples were all analyzed first, followed by the brominated samples. The brominated samples were then analyzed in order of increasing mercury levels. Apparently, the degradation of catalyst only occurred with the brominated sorbent tubes in this part of the study. The higher level brominated samples were the ones with the lowest recoveries, apparently as the catalyst trap deteriorated. The normal life expectancy for a LECO AMA 254 Mercury Analyzer is 500 runs. The lab analysts in this study recommended replacing the catalyst after no more than 250 runs with brominated sorbents.



Figure 7-2 Percent Recoveries of Mercury in lodated Sorbent Tubes



Figure 7-3 Percent Recoveries of Mercury in Brominated Sorbent Tubes

Figure 7-4 shows the percent relative standard deviations (% RSD) for the analysis of the spiked sorbent tubes. Even with the high values for the 41.3 ng set of data for the brominated sorbent by DCA and the 20.9 ng set of data for the brominated sorbent by TD, the % RSDs for the iodated and brominated sorbent samples are less than half those reported for the 40 ng spike level samples analyzed in a previous study (2). In the previous EPRI study (2) about 40 ng of mercury were spiked onto Appendix K sorbent tubes with about 2 g of iodated carbon. The amount of iodated and brominated sorbents used in the current study was about 0.2 g, or one-tenth as much. The amount of mercury used in both studies was about the same. If there were no interferences from the extra carbon in the 2 g samples, then the % RSD differences observed between the two studies would be comparable.

The earlier study indicated a possible interference from the extra carbon in the EPA Draft 324 Method during the extraction process. The direct combustion process (DCA) involved the homogenation and subsampling of the 2 g samples. This procedure may have contributed some variance to the overall process, but the magnitude of the contribution has not been determined. Calibration of the instrument used in the thermal desorption process (TD) is dependent on the mass of carbon sorbent used. The variance this contributes to the overall process has not been determined. It can be speculated that the decrease in the % RSDs is an indication of improved precision over previous studies in the measurement of low levels of mercury in sorbent tubes, keeping in mind the differences in the amount of carbon used may also be a cause of poorer precision in previous studies.

The analysis of the back sections of the spiked sorbent tubes provided additional information on the method performance. The average mercury values in the B sections are listed in Table 7-5. The 20.9 ng Hg^0 values for the Draft EPA Method 324 are those listed for the method detection limits in Table 7-3. Although the values listed for the other two methods, DCA and TD, are higher than those listed for these methods, the difference is not significant. This indicates there is very little evidence of breakthrough into the back sections during the spiking process. The insignificant difference and the small standard deviation values also indicate the measured low values of mercury are easily obtainable and in a repeatable fashion by the three analytical methods.



Analysis Method and Sorbent Material

Figure 7-4 Percent RSDs for the Determination of Mercury in lodated and Brominated Sorbent

	loc	lated Sorb	ent		Bron	ninated Sc	orbent
Method	324	DCA	TD		324	DCA	TD
		Aver	age Hg (ng	g)			
20.9 ng Hg° Spike	0.63	0.12	0.40		0.89	0.46	0.47
41.3 ng Hg° Spike	0.59	0.27	0.52		1.08	0.63	0.69
80.3 ng Hg° Spike	0.72	0.61	0.26		0.85	1.13	0.45
	Av	verage Star	ndard Devi	ation (ng)		
20.9 ng Hg° Spike	0.26	0.04	0.48		0.19	0.32	0.42
41.3 ng Hg° Spike	0.24	0.14	0.36		0.30	0.26	0.45
80.3 ng Hg° Spike	0.33	0.29	0.38		0.24	0.41	0.38

 Table 7-5

 Statistical Comparisons for B Sections of Spiked Sorbent

HgCl₂ Analytical Bias Test

The HgCl₂ analytical bias test was performed by depositing different amounts of aqueous standard HgCl₂ solutions onto bulk sorbent and determining the mercury in the sorbent by the different analytical methods. The labs submitted results for 10 replicates prepared with two different sorbents spiked at 3 (or more) levels. The average percent recoveries of mercury for each of the spike levels, sorbents, and analytical method are illustrated in Figure 7-5.

The percent recoveries in the $HgCl_2$ analytical bias test ranged from 96% to 112% for all samples and methods. Only the 10 ng iodated sample analyzed with DCA had a recovery (112%) outside the 90 to 110% acceptance range. The percent recoveries for all methods were about the same for the other concentration and methods. There was no significant difference between the results for the iodated and brominated sorbents.

Table 7-6 compares the average percent recoveries for all spike levels in the Hg⁰ and HgCl₂ analytical bias tests. The lowest and highest percent recoveries for the entire group occurred for the Hg⁰ spikes with brominated sorbents. The lowest recoveries occurred with the DCA method when the catalyst in the LECO AMA 254 Mercury analyzer appeared to deteriorate toward the end of the analyses, as discussed in Section 5.6. The highest percent recoveries occurred for the Draft EPA Method 324 analyses of the spiked samples in the brominated sorbent, likely due to unresolved matrix interferences. The analysis of the same instruments, same operator, and most of the time on the same day as the samples in the iodated sorbents. The only apparent difference between the two sets of data was the type of sorbent used.



Figure 7-5 Percent Recoveries in the HgCl₂ Bias Test

 Table 7-6

 Hg⁰ and HgCl₂ Analytical Bias Test Results

		Iodated Sorbent			Brominated Sorbent		
	Method	324	DCA	TD	324	DCA	TD
Average % Recovery		100.5	101.3	100.8	113.5	88.1	99.4
Average % RSD		5.27	5.65	4.88	3.46	8.28	6.78
Average % Recovery		96.9	103.9	98.1	101.2	102.1	101
Average % RSD		1.78	0.691	3.99	2.64	3.33	2.8

The average percent RSDs for the HgCl₂ bias test are about half those for Hg⁰ bias test. The spiked samples for the Hg⁰ bias test were prepared by the URS Corporation and distributed to the labs. The samples for the HgCl₂ bias test were prepared by each of the labs using standard mercury solutions prepared by the labs. The Hg⁰ samples had considerably more sample preparation and handling during the overall process. The glass wool had to be removed from the trap, then the sorbent removed and either placed in a boat, ladle, or digestion vessel. With the

 $HgCl_2$ bias test the sorbent is simply added to the appropriate vessel and then spiked with the solution. The percent RSDs for the Hg^0 Bias test spikes is thus a combination of the variances in the spiking, handling and analysis processes. Higher variances in the Hg^0 bias test could be due to the spiking and handling processes, since the actual instrumental analyses would be common to samples in both tests. As previously stated, the average percent RSDs for all samples and all sorbents are much lower than those obtained in previous studies for samples with similar concentrations (2,3).

Target Sample Volume

Each study participant was encouraged to calculate a target sample volume for one or more power plants. This was to be done by taking the minimum sample mass determined in Section 5.4 and using it to calculate, for each analytical technique used, the minimum sample volume required for the to obtain that mass (loading) on the sorbent trap. This step is necessary to determine an appropriate sampling duration and flow rate for planning RATA or emissions test.

Table 7-7 shows the minimum sample volumes calculated for the three analytical methods and for a relatively low $(0.3 \ \mu g/m^3)$ and moderate $(5 \ \mu g/m^3)$ emission level. The calculations are for the minimum sample mass values listed in Table 7-3. For example, for an MSM of 10 ng Hg, the following calculations give the Minimum Sample Volume (MSV):

MSV = 10 ng x 1 m³/0.3 μ g x 1 μ g/1000 ng x 1000 L/1 m³ = 33.3 L

Assuming a sampling flow of 400 cc/min, the minimum sample volumes listed in Table 7-7 would produce the minimum sampling times shown.

		lodated Sor	rbent		В	rominated S	orbent
Method	324	DCA	TD		324	DCA	TD
Minimum Sample Mass (MSM), ng Hg	10	2.8	20		2.5	3.0	20
		0.3 µg/	/m³ emissio	n level			
Minimum Sample Volume, L	33	9.3	67		8.3	10	67
Minimum Sampling Time, min	83	23	167		21	25	167
		5 µg/r	m ³ emission	level			
Minimum Sample Volume, L	2.0	0.56	4.0		0.50	0.60	4.0
Minimum Sampling	5	1.4	10		1.3	1.5	10

Table 7-7					
Minimum Sam	ple Volumes for	Low and	Moderate	Emitting	Units

8 METHOD 30B STUDY: CONCLUSIONS

The laboratories participating in this study were able to accomplish the goals of the project using the three analytical methods: Draft EPA Method 324, Direct Combustion Method and Thermal Desorption. The goals were to determine the parameters or perform the tests summarized in using the three methods. The acceptance criteria and results of this study are listed in Table 8-1.

Not all of the method criteria were met by the laboratories participating in this study. In the instances where the procedures failed to meet criteria, valuable lessons were learned concerning particular methods, sorbents, and analytical instruments. In particular, the study pointed out the need for laboratories to gain experience in applying their method of choice to a particular sorbent, and to perform the analytical matrix interference test and analytical bias tests well in advance of the need to analyze RATA samples.

Other observations about the study and the data reported are as follows:

- The method detection limits for the three methods and two sorbents were less than 1 ng mercury, with the exception of the Thermal Desorption Method (which was 1.55 ng mercury) using a brominated sorbent.
- In the analytical matrix interference test using Draft Method 324, dilution of the extracts showed a minimum dilution of about 20 is needed to minimize the iodine interference when using iodated sorbents. Interferences (unknown) with brominated sorbents are less and the level of dilution selected for use in the study was not the optimum one.
- The Hg^o bias test data submitted for the three methods was quite good compared to previous studies conducted by EPRI on Appendix K tubes. The percent recoveries for iodated sorbent ranged from 96-109%. The percent recoveries for the brominated sorbent ranged from 85-118%. The low values for this sorbent were attributed to a failing catalyst in the direct combustion method and an undetermined interference with the brominated sorbent using Draft Method 324. The % RSDs for the analyses are about half those observed in earlier studies.
- The percent recoveries for HgCl₂ bias test data ranged from 96 to 112% with % RSDs similar to those obtained in the Hg⁰ bias test. Only one spike level in the iodated sorbent using the DCA method was above the 110% acceptance criteria.
- Values for the target sample volumes for different power plants are fairly straight- forward, once the minimum sample mass for the analytical method used is known.

Table 8-1Summary of Required Procedures and Calculations

Parameter or Test	Acceptance Criteria	Results	Comments	
Method Detection Limit	Determined by EPA Method 301 or equivalent procedure	Labs determined MDL using replicate blank analyses. Thermal and Direct Combustion methods used sorbent material and 324 used Section B samples as blanks.	Laboratory requested clarification on procedure for MDL calculation for acid extraction methods.	
Analytical matrix interference test (only for wet chemical analysis)	Establish minimum dilution needed to eliminate sorbent matrix interferences	Iodated sorbent dilution met requirements of method.	Brominated sorbent dilution curve was complex, causing	
		Brominated sorbent dilution was above method acceptance criterion.	difficulty in selecting correct dilution.	
Multipoint analyzer calibration	Each analyzer reading within $\pm 10\%$ of true value and $r^2 \ge 0.99$	Criterion met for all three methods		
Analysis of independent calibration standard	Within $\pm 10\%$ of true value	Criterion met for all three methods		
Minimum Sample Mass from	MSM = 2 x Lowest Calibration Mass	MSM established for		
Lowest Calibration Mass or Concentration	(DCA and TD) or $MSM = 2 \times Lowest$ Calibration Concentration (324)	324, DCA and TD methods		
Section B Breakthrough	< 10% of MSM for Hg emissions > 1 µg/dscm	Calculated values for 324 and TD met criteria;	An increase in MSM is needed for DCA method	
	< 20% of MSM for Hg emissions $\leq 1 \mu g/dscm$	Half of the values for DCA did not meet criteria		

Table 8-1 (continued)Summary of Required Procedures and Calculations

Parameter or Test	Acceptance Criteria	Results	Comments
Analytical bias test for Hg ⁰	Average recovery between 90% and 110% at each of the three spike levels	Iodated sorbent: criterion met at all spike levels and all methods.	Catalyst degradation suspected for DCA method.
		Brominated sorbent: criterion met for TD method. For DCA, failed (low) at 2 spike levels. For Method 324, failed (high) at all 3 spike levels.	Incorrect dilution selection is suspected in failure of Method 324 test for brominated sorbent.
Analytical bias test for HgCl ₂	Average recovery between 90% and 110% at each of the three spike levels in iodated sorbent	Iodated sorbent: criterion met except for DCA, which failed high at lowest spike level.	
		Brominated sorbent: criterion met at all spike levels and all methods.	
Minimum Sample Volume, L	Calculated from MSM and emission level	Calculated for low and moderate emitting power plant units	
Minimum Sampling Time, min	Calculated from Minimum Sample Volume and 400 cc/min flow rate	Calculated for low and moderate emitting power plant units	

Some suggestions for improving the analysis of the spiked carbon sorbents in the Hg^0 and $HgCl_2$ analytical bias tests in Method 30B were offered by the analysis:

- The primary standard used to generate the calibration curve should not be an HgCl₂ standard. Instead the primary standard should be prepared from either mercury nitrate or metallic mercury.
- Begin the peak integration on the Ohio Lumex analyzer prior to inserting the ladle/sample into the analyzer furnace.

When this study was performed there was a considerable amount of difficulty in understanding the directives and procedures for the various tests outlined in Method 30B. The lab analysts only had the Draft of Method 30B and were sometimes confused by the directions. Some measurements were not performed as required. The Final version of Method 30B has more examples of the data needed, calculations involved and sample results, which is helpful in understanding the procedures. It is hoped the document can be further revised to include more examples and descriptions of terms and procedures. In particular, the participants found the application of the MDL procedure to this method to be confusing, especially for the wet chemistry methods.

Finally, it should be noted that the quality of the data reported in this study is a reflection of the quality of the laboratories and their personnel. The nature of the tests and sensitivity of the analytical procedures used are such that experienced personnel, well maintained instrumentation, and high quality laboratories are needed to accomplish the goals of this study.

9 REFERENCES

1. EPRI, 2007. Evaluation of Sorbent Materials for Flue Gas Mercury Measurement, 1014046.

2. EPA, 2007. Method 30B – Determination Of Total Vapor Phase Mercury Emissions From Coal-Fired Combustion Sources Using Carbon Sorbent Traps. http://www.epa.gov/ttn/emc/promgate/Meth30B.pdf

3. EPRI, 2007. Evaluation of Methods for Mercury Analysis of Appendix K Sorbent Traps, 10144565.

4. ASTM D 6722 – Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis and Atomic Absorption Spectroscopy, *ANNUAL BOOK OF ASTM STANDARDS*, Vol. 05.06, ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA, 2006.

5. EPA, 2007, Appendix A - Test Methods Method 301–Field Validation of Pollutant Measurement Methods from Various Waste Media. http://www.epa.gov/ttn/emc/methods/method301.html

$\ensuremath{\boldsymbol{A}}$ mass balance results for effect of SO_ tests

Table A-1 summarizes the total % recovery of pre-spiked Hg across each sorbent trap/solution unit per sorbent for each SO₂ gas condition. Replicate tests were performed for each sorbent/condition, and the recovery results of each replicate are presented in the table.

Table A-1 Total Percent Hg Recovery Results for SO₂ Gas Condition

Test (ppm SO₂)	Sorbent Vendor	Impregnated Halogen	Spike Configuration	Total % Recovery of Pre-spiked Hg
200	Ohio Lumex	Iodated	Front-half	104, 110, 111, 119%
350	Ohio Lumex	Iodated	Front-half	58, 85%
500	Ohio Lumex	Iodated	Front-half	77,90%
1000	Ohio Lumex	Iodated	Front-half	79, 82, 83, 85, 87%
200	Frontier Geosciences	Iodated	Front-half	64, 81, 82, 98%
350	Frontier Geosciences	Iodated	Front-half	53, 74%
500	Frontier Geosciences	Iodated	Front-half	72, 67%
1000	Frontier Geosciences	Iodated	Front-half	not tested
200	SKC	Iodated	Front-half	65, 82, 86, 89%
350	SKC	Iodated	Front-half	70, 100%
500	SKC	Iodated	Front-half	70,76%
1000	SKC	Iodated	Front-half	not tested
200	SKC	Iodated	Batch	not tested
350	SKC	Iodated	Batch	78, 81%
500	SKC	Iodated	Batch	73, 86%
1000	SKC	Iodated	Batch	not tested
200	Sorbent Technologies	Brominated	Front-half	110, 114, 117, 122%
350	Sorbent Technologies	Brominated	Front-half	85, 89%
500	Sorbent Technologies	Brominated	Front-half	59, 85%
1000	Sorbent Technologies	Brominated	Front-half	88, 92, 94, 101, 99%

*Results were considered suspect if the % recovery of pre-spiked mercury recovered fell outside the range of 80-120%

B DETAILED RESULTS OF EFFECT OF SO₂ TESTS

Tables B-2 through B-6 summarizes the detailed results of each SO₂ condition tested. These tables show the mass of mercury measured on the pre-spiked bed and in the Method 29 (M29) catch solutions, the calculated % of pre-spiked mercury recovered on the pre-spiked bed and across each bed/solution unit, and the percent of pre-spiked mercury loss based on the mercury measured in the M29 impingers. Table B-1 is a key applicable to all five tables.

Table B-1 Key for Data Summary Tables Notes

Note	Description
1	ng of mercury spiked on trap before gas exposure testing
2	ng of mercury measured on trap at end of test using the modified 6414 wet digestion method
3	Total % mercury of pre-spiked mercury measured post exposure to flue gas on bed 3 calculated by: (measured mercury / theoretical spike mass) *100
4	ng of mercury measured in Method 29 catch solutions post gas exposure test
5	Total % pre-spiked mercury recovered across each bed/solution unit calculated by: (ng mercury on bed 3 + ng mercury in catch solutions)/theoretical spike mass *100
6	Total % pre-spiked mercury recovered from the M29 catch solutions calculated by: (ng mercury in catch solutions/theoretical spike mass)*100
7	Halogen catch solution was placed downstream and mercury measurement was not performed
*	Below the method detection limit of approximately 900ng.
**	mercury levels were below the analytical detection limit

Table B-2 Summary of Results from the 200 ppm SO $_{\!_2}$ Gas Exposure Test

Sorbent Vendor	Impregnated Halogen	Spike Configuration	Replicate	Bed 3 spike ng Hg ¹	Bed 3 measured ng Hg²	Total % Hg recovery from Bed 3 ³	M29 catch solutions measured ng Hg⁴	Total % Hg recovered⁵	Total % loss (M29 catch solutions) ⁶
Ohio Lumex	Iodated	single trap	1	40,000	47,474	119%	BD*	119%	no loss**
Ohio Lumex	Iodated	single trap	2	40,000	41,776	104%	BD*	104%	no loss**
Ohio Lumex	Iodated	single trap	3	40,000	44,324	111%	BD*	111%	no loss**
Ohio Lumex	Iodated	single trap	4	40,000	44,002	110%	BD*	110%	no loss**
Frontier Geosciences	Iodated	single trap	1	40,000	32,256	81%	BD*	81%	no loss**
Frontier Geosciences	Iodated	single trap	2	40,000	32,942	82%	BD*	82%	no loss**
Frontier Geosciences	Iodated	single trap	3	40,000	25,466	64%	BD*	64%	no loss**
Frontier Geosciences	Iodated	single trap	4	40,000	39,200	98%	BD*	98%	no loss**
SKC	Iodated	single trap	1	40,000	32,956	82%	BD*	82%	no loss**
SKC	Iodated	single trap	2	40,000	34,440	86%	BD*	86%	no loss**
SKC	Iodated	single trap	3	40,000	25,844	65%	BD*	65%	no loss**
SKC	Iodated	single trap	4	40,000	35,588	89%	BD*	89%	no loss**
Sorbent Technologies	Brominated	single trap	1	40,000	45,444	114%	BD*	114%	no loss**
Sorbent Technologies	Brominated	single trap	2	40,000	48,790	122%	BD*	122%	no loss**
Sorbent Technologies	Brominated	single trap	3	40,000	43,988	110%	BD*	110%	no loss**
Sorbent Technologies	Brominated	single trap	4	40,000	46,648	117%	BD*	117%	no loss**

Note: see Table B-1 for definitions of superscripts.

Table B-3 Summary of Results from the 350 ppm SO $_{\!_2}$ Gas Exposure Test

Sorbent Vendor	Impregnated Halogen	Spike Configuration	Replicate	Bed 3 spike ng Hg¹	Bed 3 measured ng Hg²	Total % Hg recovery from bed 3 ³	M29 catch solutions measured ng Hg⁴	Total % Hg recovered⁵	Total % loss (M29 catch solutions) ⁶
Ohio Lumex	Iodated	single trap	1	40,000	33,519	84%	NM ⁷	-	no loss**
Ohio Lumex	Iodated	single trap	2	40,000	23,318	58%	BD*	58%	no loss**
Ohio Lumex	Iodated	single trap	3	40,000	34,075	85%	BD*	85%	no loss**
Frontier Geosciences	Iodated	single trap	1	40,000	21,298	53%	BD*	53%	no loss**
Frontier Geosciences	Iodated	single trap	2	40,000	29,517	74%	BD*	74%	no loss**
Frontier Geosciences	Iodated	single trap	3	40,000	28,608	72%	NM ⁷	-	no loss**
SKC	Iodated	SKC, batch	1	60,000	41,637	69%	4,969	78%	8
SKC	Iodated	SKC, batch	2	60,000	42,369	71%	6,491	81%	11
SKC	Iodated	SKC, batch	3	60,000	43,354	72%	NM ⁷	-	no loss**
SKC	Iodated	single trap	1	40,000	38,241	96%	NM ⁷	-	no loss**
SKC	Iodated	single trap	2	40,000	27,851	70%	BD*	70%	no loss**
SKC	Iodated	single trap	3	40,000	39,946	100%	BD*	100%	no loss**
Sorbent Technologies	Brominated	single trap	1	40,000	28,873	72%	NM ⁷	-	no loss**
Sorbent Technologies	Brominated	single trap	2	40,000	34,125	85%	BD*	85%	no loss**
Sorbent Technologies	Brominated	single trap	3	40,000	35,640	89%	BD*	89%	no loss**

Note: see Table B-1 for definitions of superscripts.

Table B-4 Summary of Results from 500 ppm SO $_{\rm 2}$ Gas Exposure Test

Sorbent Vendor	Impregnated Halogen	Spike Configuration	Replicate	Bed 3 spike ng Hg¹	Bed 3 measured ng Hg ²	Total % Hg recovery from bed 3 ³	M29 catch solutions measured ng Hg⁴	Total % Hg recovered⁵	Total % loss (M29 catch solutions)⁵
Frontier Geosciences	Iodated	single trap	1	40,000	28,621	72%	BD*	72%	no loss**
Frontier Geosciences	Iodated	single trap	2	40,000	26,714	67%	BD*	67%	no loss**
Frontier Geosciences	Iodated	single trap	3	40,000	21,766	54%	NM ⁷	-	no loss**
SKC	Iodated	SKC, batch	1	60,000	37,446	62%	14,327	86%	24%
SKC	Iodated	SKC, batch	2	60,000	35,400	59%	8,378	73%	14%
SKC	Iodated	SKC, batch	3	60,000	29,492	49%	NM ⁷	-	no loss**
SKC	Iodated	single trap	1	40,000	28,141	70%	BD*	70%	no loss**
SKC	Iodated	single trap	2	40,000	30,401	76%	BD*	76%	no loss**
SKC	Iodated	single trap	3	40,000	19,998	50%	NM ⁷	-	no loss**
Sorbent Technologies	Brominated	single trap	1	40,000	33,886	85%	BD*	85%	no loss**
Sorbent Technologies	Brominated	single trap	2	40,000	23,697	59%	BD*	59%	no loss**
Sorbent Technologies	Brominated	single trap	3	40,000	33,886	85%	NM ⁷	-	no loss**
Ohio Lumex	Iodated	single trap	1	40,000	30,982	77%	BD*	77%	no loss**
Ohio Lumex	Iodated	single trap	2	40,000	36,070	90%	BD*	90%	no loss**
Ohio Lumex	Iodated	single trap	3	40,000	32,913	82%	NM ⁷	-	no loss**

Note: see Table B-1 for definitions of superscripts.

Table B-5Summary of Results from 1000 ppm SO2 Gas Exposure Test

Sorbent Vendor	Impregnated Halogen	Spike Configuration	Replicate	Bed 3 spike ng Hg¹	Bed 3 measured ng Hg²	Total % Hg recovery from bed 3 ³	M29 catch solutions measured ng Hg⁴	Total % Hg recovered⁵	Total % loss (M29 catch solutions)⁵
Ohio Lumex	Iodated	single trap	1	40,000	12,925	32.3%	20,155	83%	50%
Ohio Lumex	Iodated	single trap	2	40,000	24,241	60.6%	7,523	79%	19%
Ohio Lumex	Iodated	single trap	3	40,000	24,628	61.6%	8,312	82%	21%
Ohio Lumex	Iodated	single trap	4	40,000	32,432	81.1%	1,484	85%	4%
Ohio Lumex	Iodated	single trap	5	40,000	20,512	51.3%	14,371	87%	36%
Sorbent Technologies	Brominated	single trap	1	40,000	39,691	99%	BD*	99%	no loss**
Sorbent Technologies	Brominated	single trap	2	40,000	40,489	101%	BD*	101%	no loss**
Sorbent Technologies	Brominated	single trap	3	40,000	36,649	92%	BD*	92%	no loss**
Sorbent Technologies	Brominated	single trap	4	40,000	35,009	88%	BD*	88%	no loss**
Sorbent Technologies	Brominated	single trap	5	40,000	37,423	94%	BD*	94%	no loss**

C METHOD 30B EVALUATION DATA

Hg(0) Bias Tests - Iodated Carbon Results

C -11-1	TD(1)			Ν	Aethod 324	Ļ			DCA				TD(2)			
Spike ng Hg	ng Hg	Average	Std Dev	% RSD	ng Hg	Average	Std Dev	% RSD	ng Hg	Average	Std Dev	% RSD	ng Hg	Average	Std Dev	% RSD
					19.65				23.46				22			
					21.03				21.57				22			
					21.85				21.44				22			
					22.22				20.16				21			
					19.53				20.79				23			
	22.7				21.54				21.82				22			
	22.8				18.91				20.52				22			
	22.6				18.33				18.55				20			
	22.5				20.33				22.56				22			
20.87	22.9	22.7	0.158	0.697	20.54	20.39	1.289	6.319	22.35	21.32	1.393	6.535	22	21.8	0.789	3.618
					39.17				45.00				42			
					44.52				42.92				43			
					44.20				41.58				42			
					42.54				41.15				43			
					42.79				41.28				41			
	43.3				38.63				41.55				43			
	43.2				41.91				40.28				39			
	43.8				43.04				35.91				42			
	42.6				43.64				40.89				40			
41.3	43.4	43.26	0.434	1.002	38.17	41.86	2.350	5.615	39.88	41.04	2.312	5.632	45	42	1.700	4.047
					81.12				84.42				78			
					83.38				84.33				78			
					78.72				79.56				76			
					79.23				77.92				72			
					81.12				79.33				79			
	83.4				82.45				83.87				86			
	80.6				80.84				91.05				76			
	84.1				90.14				81.50				84			
	80.1				81.40				79.73				77			
80.3	79.2	81.48	2.146	2.634	83.22	82.16	3.186	3.877	79.19	82.09	3.938	4.797	67	77.3	5.397	6.981

Hg(0) Bias Tests - Brominated Carbon Results

Spiko	TD(1)				Method 324				DCA				TD(2)			
ng Hg	ng Hg	Average	Std Dev	% RSD	ng Hg	Average	Std Dev	% RSD	ng Hg	Average	Std Dev	% RSD	ng Hg	Average	Std Dev	% RSD
					23.46				19.34				20			
					24.09				16.42				20			
					23.70				20.66				21			
					23.19				19.79				21			
					23.13				20.23				17			
	22.1				23.03				20.24				24			
	21.9				23.35				20.57				21			
	21.6				22.69				19.52				26			
	22.3				23.36				19.10				22			
20.87	22.5	22.08	0.349	1.58	22.29	23.23	0.504	2.17	19.56	19.54	1.216	6.22	23	21.5	2.461	11.45
					49.77				39.52				40			
					46.96				27.66				40			
					48.32				32.96				39			
					49.85				35.27				38			
					47.49				34.55				40			
	42.8				56.91				Lost sample				39			
	43.6				49.98				34.42				39			
	43.4				47.84				35.09				37			
	42.1				47.01				42.58				43			
41.3	42.4	42.86	0.639	1.49	47.11	49.12	2.990	6.09	33.05	35.01	4.186	11.96	40	39.5	1.581	4.00
					91.00				66.58				85			
					90.34				80.51				78			
					87.13				70.34				75			
					86.05				65.87				77			
					86.56				70.19				76			
	81.6				87.00				68.41				83			
	81.7				89.42				68.82				78			
	81				90.23				66.59				78			
	81.2	A			87.20				63.41				85			
80.3	79.9	81.08	0.719	0.89	90.23	88.52	1.887	2.13	68.18	68.89	4.587	6.66	84	79.9	3.900	4.88

Brominated Carbon Results for Blanks

Iodated Carbon Results for Blanks

	324		DCA				324		DCA		TD
	ng Hg						ng Hg				
	0.68		0.78		1		0.35		0.18	0.12	1.4
	0.81		0.70		0.2		0.43		0.09		0.1
	0.81		0.70		0.4		0.48		0.11		0.6
	0.80		0.76		-0.4		0.55		0.12		-0.2
	0.00		0.51		1		1 30		0.10		0.2
	0.71		0.51		0.4		0.61		0.19		0.0
	0.82		0.51		0.4		0.61		0.10		-0.1
	0.97		-0.09		0.2		0.65		0.10		0.5
	0.90		0.45		0.6		0.67		0.09		0.7
	1.29		-0.10		0.7		0.61		0.11		0
	1.15	0.89	0.43	0.46	0.6	0.47	0.62	0.63	0.13	0.12	0.4
	1.03		1.05		1.1		0.27		0.63		0.4
	0.73		0.54		0.2		0.26		0.31		0.7
	0.72		0.96		0.6		0.41		0.21		0.9
	1.07		0.85		0.7		0.52		0.36		0.5
	1.40		0.68		0.8		0.51		0.18		0.6
	0.89		0.67		12		0.60		0.17		0.3
	1.09		0.47		13		0.00		0.24		0.5
	1.08		0.47		1.5		0.77		0.24		0.0
	0.91		0.34		0.2		0.68		0.17		1
	1.32		0.40		0		0.95		0.20		-0.3
	1.63	1.08	0.35	0.63	0.8	0.69	0.89	0.59	0.23	0.27	0.5
	0.70		1.58		1		0.81		1.19		0.8
	0.80		1.64		0.4		0.86		0.92		0.2
	0.75		1.39		1.1		1.07		0.57		0.6
			1.49		0.6		1.18		0.76		0.4
	1.47		1.41		0.5		1.11		0.47		-0.2
	0.71		0.99		0.3		0.34		0.45		0.5
	0.87		0.88		0.3		0.33		0.44		0.3
	0.70		0.64		0.2		0.41		0.37		0.3
	0.02		0.64		0.2		0.41		0.37		0.5
	0.95	0.05	0.04	4.40	-0.2	0.45	0.57	0.72	0.54	0.64	-0.5
	0.77	0.85	0.67	1.15	0.5	0.45	0.54	0.72		0.01	0.2
First 10 blanks (10 ng spikes)	B sections									
Average	0.80		0.46		0.47		0.63		0.12		0.40
Standard Dov	0.05		0.70		0.47		0.05		0.12		0.40
Stanuaru Dev	0.19		0.52		0.42		0.20		0.04		0.46
Hign	1.29		0.78		1		1.3		0.19		1.4
Low	0.68		0.09		-0.4		0.35		0.09		-0.2
Second 10 blank	s (10 ng spik	es) B sectio	ons								
Average	1 08		0.63		0 69		0 59		0 27		0.52
Standard Dov	0.20		0.05		0.05		0.33		0.27		0.52
	0.50		1.05		1.2		0.24		0.14		0.30
nigii	1.4		1.05		1.5		0.95		0.05		0.9
LOW	0.72		0.34		U		0.26		0.17		-0.3
Third 10 blanks	(10 ng spikes) B section	5								
Average	0.85		1.13		0.45		0.72		0.61		0.26
Standard Dev	0.24		0.41		0.38		0.33		0.29		0.38
High	1 47		1.64		1 1		1 11		1 19		0.8
Low	0.7		0.64		-0.2		0.33		0.34		-0.5
All 30 blanks (10), 50, and 100) ng spikes)	B sections								
					0.51				0.00		
Average	0.94		0.74		0.54		0.65		0.33		0.39
Standard Dev	0.259		0.434		0.416		0.273		0.269		0.408
High	1.63		1.64		1.3		1.3		1.19		1.4
Low	0.68		-0.1		-0.4		0.26		0.09		-0.5
DCA HgCl2 Bias Test

iodated Carbon Results

Brominated Carbon Results

Spike	Mass	ng Hg	Average	Std Dev	% RSD	% Recovery	Spike	Mass	ng Hg	Average	Std Dev	% RSD	% Recovery
10 ng	0.01026	11.12	11.2	0.151	1.341	112.38	100 ng	0.00996	101.09	100.3	3.419	3.408	100.32
	0.01015	11.00						0.01024	101.78			9 3.560	
	0.01029	11.17						0.01028	103.02				
	0.01015	11.11						0.01018	96.39				
	0.01001	11.16						0.01017	100.97				
	0.01021	11.30						0.01016	105.72				
	0.01015	11.37						0.01018	103.46				
	0.01018	11.46						0.00994	96.24				
	0.01022	11.44						0.01009	98.86				
	0.01005	11.26						0.01004	95.69				
50 ng	0.01039	51.75	50.4	0.602	1.194	100.85	50 ng	0.01017	50.35	48.8	1.739	3.560	97.69
	0.01039	50.44						0.01011	49.61				
	0.01039	50.37						0.01012	49.95				
	0.01028	49.61						0.00975	48.21				
	0.01039	50.67						0.01026	51.11				
	0.01012	49.68						0.0094	47.56				
	0.01033	50.63						0.01002	50.34				
	0.01011	50.57						0.01018	48.90				
	0.01009	50.49						0.01018	46.17				
	0.01018	50.02						0.01028	46.28				
100 ng	0.0101	99.12	98.4	0.593	0.603	98.36	10 ng	0.01045	10.92	10.8	0.326	3.011	108.24
	0.01003	98.27						0.01024	10.93				
	0.01	98.38						0.01041	10.75				
	0.01027	98.20						0.01042	10.84				
	0.01016	97.74						0.0095	10.00				
	0.01	98.25						0.01034	10.93				
	0.01028	98.37						0.01057	11.27				
	0.01017	99.47						0.01025	10.92				
	0.01017	98.37						0.01002	10.74				
	0.01016	97.39						0.01023	10.95				

TD HgCl2 Bias Test

iodated	Carbon Res	ults					Brominate	ed Carbon Res	ults				
Spike	ng Hg	Area	Average	Std Dev	% RSD	% Recovery	Spike	ng Hg	Area	Average	Std Dev	% RSD	% Recovery
20 ng	19	4100	19.60	0.699	3.567	98.00	10 ng	10	2120	10.07	0.340	3.377	100.70
	20	4340						11	2340				
	19	4110						10	2100				
	20	4390						10	1990				
	19	4170						10	1970				
	21	4470						10	2120				
	20	4330						10	2070				
	19	4140						9.7	1900				
	20	4270						10	2020				
	19	4220						10	2080				
50 ng	49	10500	50.30	1.829	3.636	100.60	50 ng	49	9730	50.60	1.265	2.500	101.20
	49	10600						50	9850				
	53	11400						49	9700				
	48	10200						50	9920				
	53	11400						51	10200				
	49	10500						52	10400				
	50	10800						53	10600				
	51	11000						50	9880				
	52	11200						51	10200				
	49	10500						51	10100				
100 ng	101	21600	97.10	5.043	5.194	97.10	100 ng	97	19100	101.10	2.558	2.530	101.10
	93	19800						101	20000				
	97	20700						102	20200				
	91	19500						100	19700				
	109	23200						102	20100				
	97	20700						99	19500				
	96	20400						105	20800				
	97	20700						99	19600				
	97	20800						105	20700				
	93	19800						101	19900				
10 ng	10	2240	9.67	0.343	3.551	96.70							
	10	2140											
	9.8	2080											
	9.2	1950											
	10	2230											
	10	2330											
	9.5	2010											
	9.6	2050											
	9.5	2020											
	9.1	1940											

Brominated Carbon Results

324 HgCl2 Bias Test

Iodated Ca	arbon						Brominated	d Carbon					
Spike,							Spike,						
ng	Dilution	<u>ng Hg</u>	<u>Average</u>	Std Dev	<u>% RSD</u>	<u>% Recovery</u>	<u>ng</u>	Dilution	<u>ng Hg</u>	<u>Average</u>	Std Dev	<u>% RSD</u>	<u>% Recovery</u>
25	25	23.43	24.21	0.63	2.69	96.85	25	20	24.68	25.36	0.81	3.26	101.43
25	25	24.03					25	20	24.37				
25	25	23.84					25	20	23.99				
25	25	24.72					25	20	25.68				
25	25	23.55					25	20	24.89				
25	25	24.30					25	20	25.86				
25	25	24.53					25	20	25.93				
25	25	24.41					25	20	25.89				
25	25	25.53					25	20	25.89				
25	25	23.76					25	20	26.40				
60	50	58.50	58.97	0.89	1.53	98.28	60	50	58.95	59.86	1.19	2.01	99.77
60	50	59.50					60	50	57.82				
60	50	57.37					60	50	59.84				
60	50	60.63					60	50	61.09				
60	50	59.77					60	50	59.14				
60	50	58.99					60	50	61.99				
60	50	59.32					60	50	59.45				
60	50	58.53					60	50	59.79				
60	50	58.61					60	50	60.83				
60	50	58.47					60	50	59.71				
95	100	90.03	90.80	1.11	1.23	95.57	95	100	92.26	97.18	2.69	2.92	102.29
95	100	90.21					95	100	97.39				
95	100	88.80					95	100	93.24				
95	100	90.97					95	100	95.90				
95	100	92.26					95	100	98.70				
95	100	89.80					95	100	100.85				
95	100	91.09					95	100	99.23				
95	100	91.91					95	100	98.92				
95	100	92.09					95	100	97.21				
95	100	90.81					95	100	98.05				

C-7

Blank Data Used for MDL Calculations

DCA

TD

Iodated Sorbent

Iodated Sorbent

Mass	ng Hg	Std dev		Description	ng Hg	Area		
0.15097	0.1529	0.0262	0.0786	Blank Iodated C 150 mg	0.1	31	0.243	0.729
0.15121	0.2174			Blank Iodated C 150 mg	0.2	45		
0.15059	0.1918			Blank Iodated C 150 mg	-0.3	-54		
0.15041	0.1414			Blank Iodated C 150 mg	0.2	38		
0.15019	0.2005			Blank Iodated C 150 mg	-0.1	-20		
0.15067	0.182			Blank Iodated C 150 mg	-0.2	-48		
0.15044	0.1746			Blank Iodated C 150 mg	-0.4	-83		
0.1505	0.1541							
Brominated Sorbent			Brominated Sorbent					
0.15045	0.3227	0.0847	0.2542	Brominated C blank 150 mg	-0.2	-46	0.515	1.546
0.15082	0.2657			Brominated C blank 150 mg	0.7	145		
0.15021	0.153			Brominated C blank 150 mg	0	-2		
0.15073	0.1135			Brominated C blank 150 mg	-0.6	-110		
0.15132	0.1331			Brominated C blank 150 mg	-0.4	-75		
0.14993	0.1325			Brominated C blank 150 mg	0.7	133		
0.15014	0.1028			Brominated C blank 150 mg	0.3	54		

Note: MDL data was not provided for Method 324.

Analytical Matrix Dilution Test Data for Draft Method 324

Iodated Ca	rbon Dilut	ion Data		Brominated Carbon Dilution Data					
		% Recovery	Dilution			% Recovery	Dilution		
LFB	53.07	106.14		LFB	53.07	106.14			
100X	47.04	94.08	100						
50X	49.15	98.3	50	50X	49.48	98.96	50		
25X	49.92	99.84	25	25X	52.63	105.26	25		
20X	48.55	97.1	20	10X	54.35	108.7	10		
10X	32.05	64.1	10	5X	53.61	107.22	5		
5X	10.06	20.12	5	2X	51.75	103.5	2		

LFB = Lab Fortified Blank

Calibration Data for TD and DCA Methods

Ohio Lumex (TD)			LECO (DCA)					
lodated carbon			Iodated Carbon			Brominated Carbon		
	<u>ng Hg</u>	OL Signal		Mass, g	<u>ng Hg</u>		<u>Mass, g</u>	<u>ng Hg</u>
Std20	22	4550	502-406 (1633b Nist)	0.04973	7.0396	502-406 (1633b Nist)	0.15051	21.9713
Std60	60	12300	502-406 (1633b Nist)	0.05073	7.0586	502-406 (1633b Nist)	0.10079	15.3436
Std80	81	16600	502-406 (1633b Nist)	0.05057	6.9673	502-406 (1633b Nist)	0.101	14.9108
Std10	10	2150	502-406 (1633b Nist)	0.02495	3.4627	502-406 (1633b Nist)	0.02532	3.7377
Std100	98	20100	502-406 (1633b Nist)	0.02561	3.6342	502-406 (1633b Nist)	0.02632	3.8825
Std40	39	8130	502-406 (1633b Nist)	0.02594	3.6861	502-406 (1633b Nist)	0.02525	3.7217
40 check std HgCl2	42	8580	502-406 (1633b Nist)	0.01046	1.4383	502-406 (1633b Nist)	0.01052	1.4588
0.9856 ppm std 40 ul	36	7480	502-406 (1633b Nist)	0.0106	1.5177	502-406 (1633b Nist)	0.01038	1.4696
40 check std HgNO3	40	8280	502-406 (1633b Nist)	0.01057	1.5011	502-406 (1633b Nist)	0.01045	1.5394
			502-406 (1633b Nist)	0.10129	14.1634	502-406 (1633b Nist)	0.10061	14.8003
Brominated Carbon			502-406 (1633b Nist)	0.10043	13.8221	502-406 (1633b Nist)	0.15052	21.5466
BLANK	0	72	502-406 (1633b Nist)	0.10044	14.0679	502-406 (1633b Nist)	0.15021	21.3786
BLANK	-0.1	25	502-406 (1633b Nist)	0.15034	21.2764			
Std20	21	4300	502-406 (1633b Nist)	0.151	21.2357			
Std40	40	7890	502-406 (1633b Nist)	0.1507	21.5838			
Std60	59	11700						
Std80	81	16100	0.01046	1.4383	1.375	0.01052	1.4588	1.387
Std100	107	21100	0.0106	1.5177	1.432	0.01038	1.4696	1.416
Std100	98	19300	0.01057	1.5011	1.420	0.01045	1.5394	1.473
Std10	9.4	1840		Std dev =	0.0300		Std dev =	0.0440
20 check HgNO3	20	3950						
20 check HgCl2	20	4010						

Note: Raw calibration data were not provided for Draft Method 324 analyses

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