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Evaluation of Methods for Mercury Analysis of Appendix K Sorbent Tubes

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Technical Update, March 2007

EPRI Project Manager

N. Goodman

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ABSTRACT

Electric generating units in the United States that burn coal are required to monitor mercury emissions beginning in 2009. Sorbent tube mercury monitoring systems, as described in Appendix K to 40 CFR Part 75 (the Clean Air Mercury Rule), can fill two potential roles in mercury monitoring: as a replacement for a continuous emission mercury monitor (CEMM) in routine compliance monitoring, and as a potential reference method for relative accuracy test audits (RATA) of a CEMM. U.S. regulations do not specify the analytical procedures to be used to measure mercury in sorbent material, and few laboratories were familiar with the requirements for making these measurements. The purpose of this study was to evaluate candidate analytical methods and to evaluate the performance of those methods in multiple laboratories. Sorbent tubes packed with iodine-treated activated carbon were loaded with known amounts of mercury at concentrations that might be encountered in actual application of a sorbent tube sampling system. Laboratories participating in the study were provided assistance in setting up their equipment and learning the procedures. After an initial period of familiarization, each laboratory analyzed mercury concentrations in a set of sorbent tubes. Methods used in the study included acid extraction, direct combustion, and thermal desorption techniques, using either atomic absorption spectrometric (AAS) or atomic fluorescence spectroscopic (AFS) detectors. The resulting measurements were evaluated for method precision and accuracy, as well as comparing the results against the Appendix K quality control criteria for sorbent tube mercury systems. The results indicate that all of the methods tested can produce acceptable results, but that considerable effort is needed at the outset to optimize the method conditions for the specific instrumentation in each laboratory.

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INTRODUCTION

1.1 Background

Electric generating units in the United States that burn coal are required to monitor mercury emissions beginning in 2009. As set out in Appendix K to 40 CFR Part 75, the Clean Air Mercury Rule (CAMR), each stack must be equipped with a continuous emission monitor (CEM) for mercury and the facility must conduct annual relative accuracy test audits (RATAs) of each CEM system by comparing its performance to a reference method. The reference method currently approved by the U.S. Environmental Protection Agency (EPA) is the Ontario Hydro Method (ASTM D 6784). EPA has also proposed use of EPA Method 29 for this purpose (Federal Register, August 22, 2006), and has requested comments on the use of a sorbent tube sampling approach as an alternative reference method.

Sorbent tube mercury monitoring systems, such as the QuickSEM system developed by EPRI, can fill two potential roles in compliance with the CAMR: as a replacement for a CEM, and as a reference method for RATA testing of CEMs. QuickSEM is a semi-continuous sampling system that uses activated carbon sorbent tubes within an in-stack, dual-tube probe to collect mercury from flue gas. The tubes can be left in place for several hours up to several weeks, giving a measurement of total mercury emitted over that time period. At the end of the sampling period, the used tube is removed and sent to a laboratory for mercury analysis.

Appendix K does not specify the analytical procedures to be used to measure the trapped mercury or even the sorbent to be used; any sorbent or analytical method that can achieve quality control criteria specified in Appendix K is acceptable. At the time this project was begun, there was only one commercially available sorbent that had been demonstrated to meet the requirements of Appendix K: a proprietary, iodide-treated, activated carbon.

In the proposed CAMR, EPA described a draft analytical method for mercury in iodated activated carbon. Draft EPA Method 324 was developed by Frontier Geosciences of Seattle, Washington, with support from EPRI. It involves extraction of the mercury from the sorbent tube with acid and a strong oxidizing agent, followed by atomic fluorescence spectroscopy (AFS). This method was validated in a single laboratory according to procedures outlined in EPA Method 301. The proposed CAMR stated that other analytical methods may be acceptable.

When EPA issued the final CAMR, the regulations for mercury monitoring were made performance-based; no analytical method was specified or described in the Rule. Appendix K sets criteria for instrument calibration and for recovery of a mercury spike from the sorbent after sampling. Any method that can achieve these criteria is acceptable.

The current study was designed to evaluate the performance of available methods for analysis of mercury in iodated activated carbon, and to collect data that would assist power generating companies to begin implementing the methods, either in their own in-house laboratories, or in a contract laboratory.

1.2 Project Objectives

The primary objective of this project was to evaluate the performance of analytical methods for mercury in sorbent material, to determine whether the methods were capable of meeting the quality control requirements of Appendix K. A secondary objective was to assist participating organizations to learn to use these analytical methods and improve their performance.

At the time that Appendix K was finalized, only one method (Draft Method 324) had been demonstrated to be applicable to sorbent mercury analysis. However, the Draft Rule suggested that other techniques, including thermal desorption and acid digestion with atomic absorption spectrometric analysis (AAS) could potentially be applicable. For this study, in addition to Draft Method 324, laboratories were allowed to use modifications of several methods already in use for analysis of mercury in coal.

The project consisted of two phases: 1) a ruggedness testing/laboratory familiarization phase and 2) a round robin phase. In Phase I the participating 1abs were given written documentation and advice to familiarize their staff with the required lab procedures. The labs were then provided with iodide-treated activated carbon tubes spiked with known amounts of mercury, to allow them to evaluate their own performance on the method. Each laboratory selected the method(s) that they would test.

In Phase II, a multilaboratory round robin study was conducted to characterize the performance of several techniques for analyzing mercury in sorbent tubes. The laboratories were provided with sets of spiked tubes, but the spike concentrations were not revealed to participants until after the study was completed.

The focus of the study was to evaluate the analytical methods under carefully controlled conditions; therefore, the sorbent tubes were not exposed to flue gas. Spiking was performed by transferring mercury from a liquid medium to the sorbent tube in a mercury-free gas stream. Therefore, analytical interferences or losses of mercury spike that may occur during sampling due to the presence of other flue gas components are not reflected in this study.

It is also important to note that the mercury concentrations tested in this study do not cover the full range of concentrations that could potentially be encountered in practice. This study focused primarily on mercury loadings typical of routine compliance monitoring; for example, the amount that would be collected over one- or two-week sampling duration. Other applications of sorbent tube sampling (for example, a two-hour RATA on a low-emitting stack) could potentially trap much less mercury than the lowest spike level tested in the current study. Laboratories attempting to analyze samples with very low levels of mercury may run into limitations with instrument sensitivity and with background levels of mercury in the laboratory ambient air. The decision was made not to extend the current study to these lowest levels in order to allow participation by laboratories that were not set up for clean room, ultra-trace mercury analysis.

2
STUDY DESIGN AND METHODOLOGY

The multilaboratory study was coordinated by John T. Riley, Ph.D., under EPRI sponsorship. Sample preparation was performed by ARCADIS, and verification of sample spikes was performed by ARCADIS and Frontier Geosciences.

The study was divided into two phases: (1) laboratory familiarization and ruggedness testing and (2) a multilaboratory round robin study.

2.1 Phase I Study Design

Each laboratory that participated in Phase I received the following materials:

- 30 large, 2-section sorbent tubes, spiked with 3 levels of mercury (10 tubes per level)
- 5 unspiked (blank) tubes for use as method blanks

The Phase I samples were targeted to contain the following spikes: 300 ng, 3,000 ng, and 10,000 ng of mercury per tube. Figure 2-1 plots these target spike levels against the expected mercury loading on a tube as a function of sampling duration, assuming a typical sample collection rate of 400 cc/minute. The curves in the plot represent tube loadings at low, medium, and high mercury emission rates of 0.1, 1.0, and 10 micrograms per cubic meter ($\mu g/m^3$). The horizontal dashed lines indicate the spiking levels selected for Phase I. For example, a 3000 ng spike corresponds to about a 5-day sample on a stack that emits $1\mu g/m^3$ mercury.

The three spikes used in Phase 1 do not encompass the entire range of mercury loadings that might be seen in practice: in particular, the very low levels of mercury likely to be encountered in a RATA (e.g., a 2-hour sample) were not included in Phase 1, as it was not desirable to push the limits of the analytical methods during the familiarization process.

The Phase I samples were prepared in two batches: in the first batch, spiked in September, 2005, ARCADIS prepared sufficient samples to provide a sample set for 6 participating laboratories, verification samples, and samples for a long-term stability study. Addition of more participants and requests for additional sample sets by participating laboratories made it necessary to prepare an additional batch of samples in October 2005, along with a sample set for verification analysis. In evaluating the Phase I results, each laboratory's results were evaluated against the verification analyses for the batch that they received.

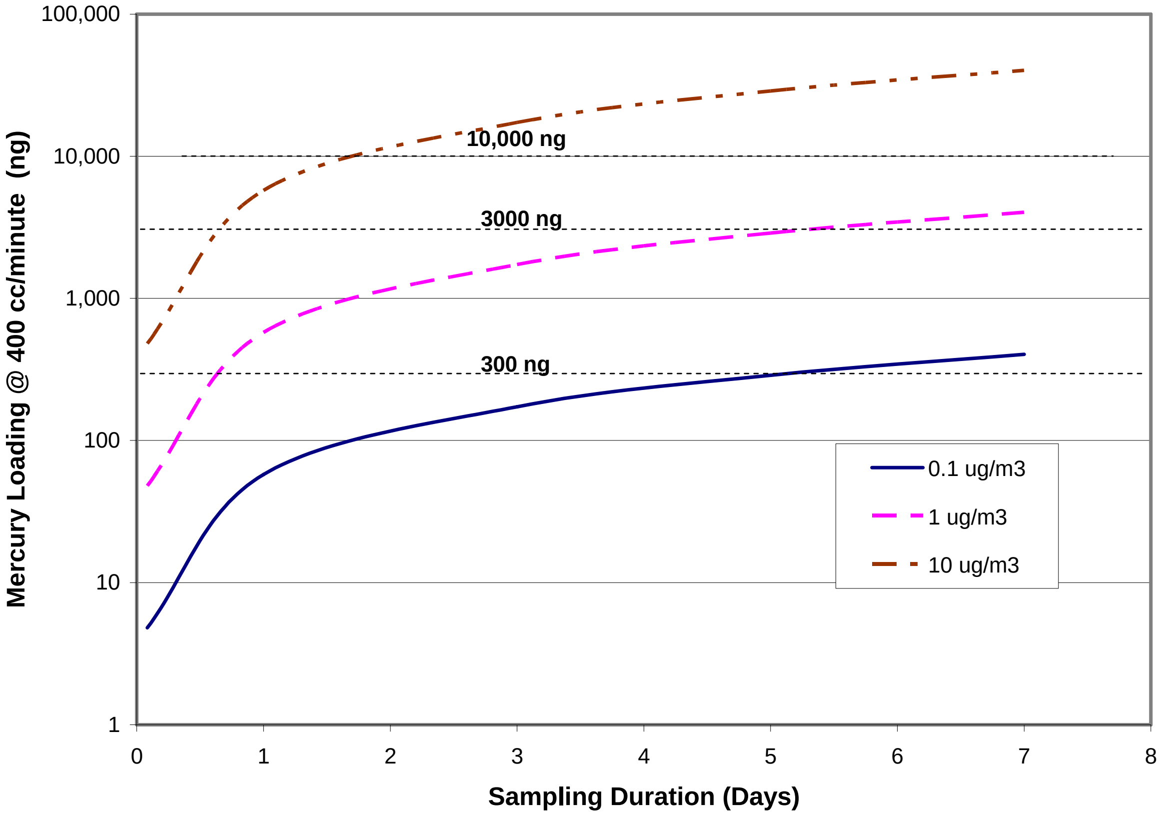

Figure 2-1
Phase I Sorbent Tube Mercury Loadings

2.2 Phase II Study Design

The objective for Phase II was to determine the performance characteristics of the analytical methods used for Appendix K mercury analysis. In particular, EPRI wished to determine whether the test methods could meet the following specific requirement of the Rule:

> "Prior to analyzing field samples and prior to use of new sorbent media, the facility must conduct a spike recovery study. The average recovery of mercury from the sorbent must be between 85% - 115% at each of 3 spike concentration levels."

In addition, the Phase II study was designed to meet the requirements of ASTM Standard Practice E 691, *Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method* (2).

Each laboratory that participated in Phase II received the following materials:

- 30 large, two-section spiked tubes (five each at six spike levels)
- two blank (unspiked) tubes for use as quality control samples

- one ampoule of trace level mercury solution for preparation of the quality control samples

In Phase II, the spike levels chosen for testing were: 40 ng, 250 ng, 2500 ng, 9000 ng, 25,000 ng, and 40,000 ng. Figure 2-2 compares these spike levels with mercury loadings from various sampling durations and stack emission rates, assuming a 400 cc/minute sampling rate. The horizontal dashed lines indicate the spiking levels selected for Phase II. As shown in this figure, a 40 ng sample corresponds to about a 2-hour sample for a stack with mercury emissions somewhat below 1 µg/m^3. A 40,000 ng sample is approximately what would be collected in a high emitting stack (10 µg/m^3) after about seven days. Lower and higher loadings could be encountered in practice; however, practical considerations limited the range of mercury loadings evaluated in this study. Analysis of lower levels would likely require a clean laboratory setup to reduce background mercury contamination, as well as requiring many of the participants to upgrade their instrumentation. Preparation of higher level spikes has been demonstrated outside of this study (up to about 100,000 ng) but spiking at this level would have greatly increased the time required to obtain complete transfer of mercury from solution.

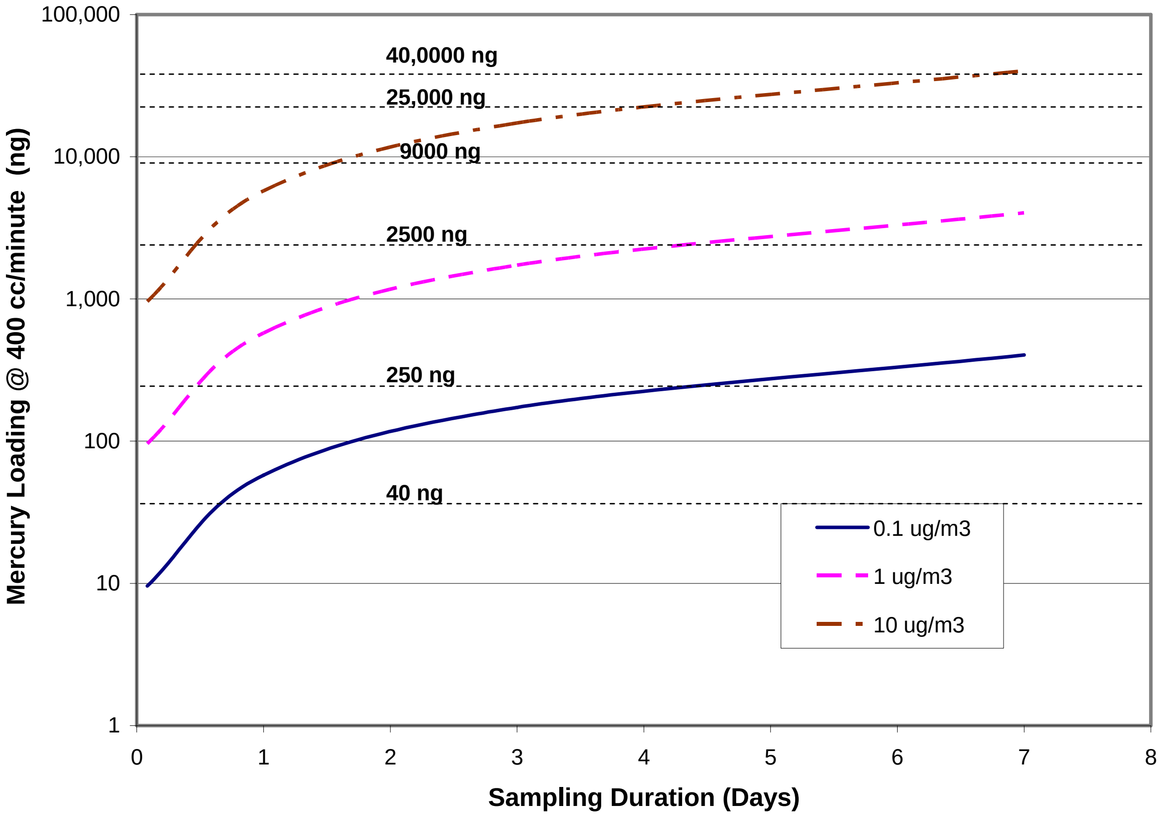

Figure 2-2
Phase II Sorbent Tube Mercury Loadings

To give adequate data for evaluation of within-lab precision, five sorbent tubes at each spike level were sent to each of the participating laboratories. Two blank sorbent tubes were sent to the laboratories to use to prepare quality control samples. The QC samples were to be prepared by adding a weighed mass of a standard reference material, 1641d, from the National Institute of Standards and Technology (NIST) to the iodide-treated carbon from the A section of the blank tubes. These samples were the best available approximation of a sorbent tube spiked with a certified value of mercury. The QC samples were used to check for any bias(es) in the analytical procedures used in the study.

2.3 Description of Carbon Tubes and Sorbent

Iodide-treated activated carbon sorbent tubes were used for this study. Large size, blank sorbent tubes were obtained from Frontier Geosciences. Figure 2-3 shows the dimensions of the large size glass tube and a picture of a tube.

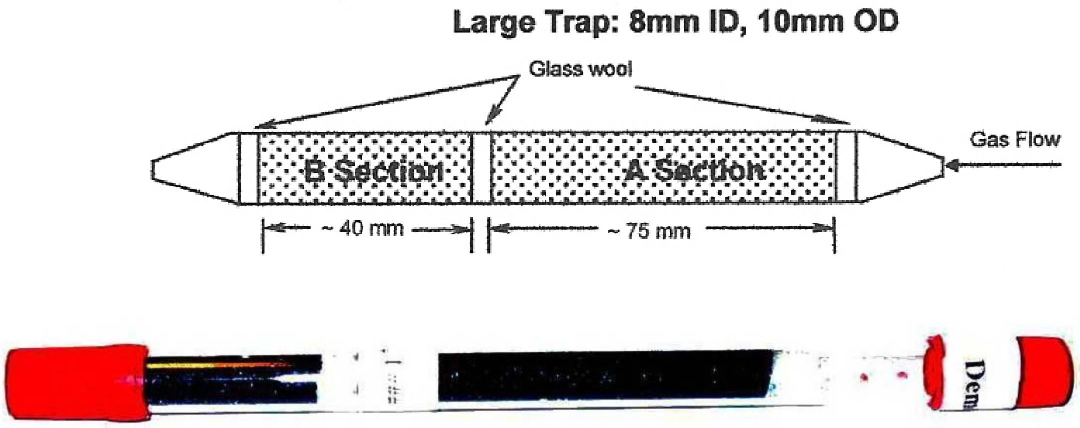

Figure 2-3
Schematic Diagram and Picture of the Large Size Sorbent Tube

The two-section sorbent tubes had approximately 1.7 grams of carbon in the A section and 0.7 grams in the B section. The A section was spiked with mercury, while the B section was used to determine breakthrough of mercury during the spiking procedure. Since there was no indication of breakthrough in any tube, the B section analysis can be considered a method blank. Frontier Geosciences has recently changed the tubes that they sell commercially: each tube now has three sections, each with 1 gram of carbon. The third section is used to comply with the Appendix K requirement to spike each tube with a known amount or mercury before it is used for stack sampling. Because EPRI’s study did not involve compliance monitoring, a three-section tube was not needed.

The iodide-treated activated carbon sorbent used in the Frontier Geosciences tubes is a very uniform material, consisting of granular particles with a diameter of 2-3 mm. The proprietary material is a coconut shell carbon; the form and concentration of iodine in the material was not provided by the supplier, but is assumed to be an iodide species rather than elemental iodine.

2.4 Spike Preparation and Verification

Spiked samples were prepared by ARCADIS. The mercury vapor used to spike the tubes was produced from a solution containing a known amount of mercuric nitrate ($Hg(NO_3)_2$) solution, to which a known amount of the reducing agent stannous chloride was added. A sorbent tube was connected to a series of fritted impingers containing the mercury solution. A vacuum was placed on the outlet of the tube to pull filtered ambient air through the mercury solution and onto the carbon sorbent.

Samples used in Phase I of the project were produced using a spiking apparatus developed in ARCADIS' laboratory. Based on the results of verification analyses of the Phase I samples (discussed in Section 3), it was determined that this apparatus was not completely transferring mercury from solution onto the sorbent tubes. EPRI decided to proceed with Phase I using these spiked tubes, which contained between 75% and 85% of the intended loading. However, prior to Phase II, ARCADIS was asked to modify their spiking apparatus and to verify that complete transfer could be obtained. The modified apparatus was demonstrated to produce acceptable transfer at tube loadings between 100 ng and 20,000 ng of mercury. The improvements to the procedure involved changing to a bubbler with a smaller frit size and decreasing the stannous chloride concentration. The earlier apparatus apparently did not produce small enough bubbles with enough surface area to transfer the mercury within a 30-60 minute period.

Four of the new spiking systems were set up, so that four tubes could be spiked at a time. This allowed for efficient production of large numbers of spiked samples for the study. The tubes were numbered sequentially on the outside of the tube to allow tracking, and tube numbers were randomly assigned to participants, to avoid systematic error in case of any temporal bias in the spiking process. After each tube was spiked, it was capped, and the tubes stored in ziploc bags. The spiked samples were stored at room temperature in a mercury free area until they were shipped. Details of the spiking procedure, along with pictures of the spiking apparatus, are given in Appendix A.2.

Analytical data from two laboratories was used to verify the amounts of mercury deposited on the iodide-treated activated carbon in the sorbent tubes. Frontier Geosciences used Draft EPA Method 324, while ARCADIS used an Ohio Lumex mercury analyzer, which uses a thermal desorption procedure, for in-house analysis. Several sets of samples were used for spike verification during Phase I and II. These data are presented and discussed in later sections on verification analysis.

2.5 Laboratories

The following laboratories participated in the study:

- AAL Laboratory
- American Electric Power (AEP) Dolan Laboratory
- Alabama Power
- Consumers Energy
- Eon US
- First Energy
- LECO Corporation
- Tennessee Valley Authority

2.6 Selection of Test Methods

At the beginning of this project, each participating laboratory was asked to evaluate the suitability of Draft EPA Method 324 for use in their laboratory, and to also investigate the possible use of other methods. Only one of the laboratories had been routinely using Draft Method 324; they did not participate in Phase I of the project. A second laboratory elected to use Draft Method 324. Other laboratories had been routinely analyzing mercury in coal using ASTM Method 6414 (2), but had limited or no experience with analyzing mercury in the sorbent tube material. Most of these labs elected to attempt to modify the ASTM method rather than adopt Draft Method 324.

Selection of methods was influenced by the equipment available in each laboratory; labs that owned AAS instruments but did not own AFS were generally not interested in purchasing a new instrument if it was not necessary. One laboratory was interested in using thermal desorption, due to its adaptability to quick-turnaround analysis at a power plant location. Another participant, an instrument manufacturer, used their own direct combustion/AAS instrument in the study.

Another consideration for those laboratories that elected not to use Draft Method 324 was the relative hazard of the reagents compared to those required for other acid extraction methods. As discussed below, Draft Method 324 requires the use of bromine monochloride, a relatively unstable oxidizing agent that has a tendency to form bubbles and foam when it is added to the acid extract solutions. The possible release of noxious bromine from solutions of this reagent was also a concern.

As an outcome of this decision process, the methods selected for use in Phase I were as follows:

- Draft EPA Method 324/AFS (one laboratory)
- Modified ASTM Method D 6414 – Acid Extraction/AAS or AFS (five laboratories)
- Thermal Desorption/AAS (one laboratory)
- Direct Combustion Analysis/AAS - Modified ASTM Method D 6722 (one laboratory)

Several laboratories used more than one method to analyze the samples, either by analyzing the acid extracts using multiple instruments, or by analyzing several complete sample sets by different methods.

The only change in methods used during Phase II was that one additional laboratory participated, using Draft Method 324.

2.7 Description of Study Procedures and Test Methods

Participants were supplied with a set of capped tubes stored in sealed plastic bags. Each tube had two sections of carbon, held in place with glass wool. To extract the activated carbon, the tubes were opened and the sorbent beds and glass wool packing material placed in a trace-clean vessel. The tube was cut using a tube cutter, dremel, or other cutting device. and the glass wool carefully removed using a pick tool. The carbon was then carefully transferred to a digestion vessel for wet chemistry analyses, or directly to the sample ladle for Ohio Lumex analyses, making sure that none of the carbon particles were lost. The glass wool plug was added to the digestion vessel for wet chemistry analyses. For the Ohio Lumex analyses the glass wool plug was wrapped in aluminum foil and analyzed separately

The design of the sorbent tube and the dynamics of the spiking procedure result in most of the mercury being trapped at the front of the A section of the sorbent tube. This means the sorbent mercury concentration is quite heterogeneous; a very small number of carbon particles contain most of the mercury. This heterogeneity had to be dealt with in removing the sorbent material from the tube so that no particles are lost in the transfer.

There was considerable interest among the participants in homogenizing the carbon so that multiple analyses could be conducted on subsamples of carbon. Homogenation would allow users of instruments such as the Ohio Lumex, which consumes the entire sample, to perform repeated analyses of a sample and so lower the risk of data loss from an unsuccessful instrument run. However, an initial trial of methods to homogenize and split the sample of sorbent material met with failure to obtain representative splits. For this reason, participants using acid extraction techniques were requested to extract the entire tube section.

Several of the methods used in the study could not accommodate an entire sorbent tube section (1.7 grams in the A section and about 0.7 grams in the B section). The Ohio Lumex sample ladle holds only one gram, and the LECO analyzer typically is run with 100-200 milligrams of solid material. The solution to this problem was for Ohio Lumex to split the A section into two test runs and sum the results. LECO used a ball mill to homogenize the carbon in each tube, which did allow for repeat analysis.

The analytical methods used in the study are described below.

Draft EPA Method 324

This method was described in the proposed CAMR, but was never finalized and is not currently recognized as an official method by EPA. The full title of the method is: *Draft Method 324 – Determination of Vapor Phase Flue Gas Mercury Emissions from Stationary Sources Using Dry Sorbent Tube Sampling – Subsection: Analysis Method by CVAFS*. A detailed procedure for the draft method, prepared by Frontier Geosciences, is given in Appendix A.2.

In this method, the solid sorbent material is extracted in hot concentrated nitric/sulfuric acid mixture, the solution filtered, and the extract diluted with bromine chloride (BrCl) before analysis by AFS. Highlights of the analytical procedure are as follows:

- A 70:30 ratio mixture of HNO_3:H_2SO_4 is added to the solid sorbent (entire sample of ~1.7 g) at a 35:1 acid:carbon ratio in a digestion bottle with a tight fitting cap.
- The mixture is heated at 50-60°C for 1.5 to 2 hours.
- After cooling to room temperature, a 5% solution of BrCl is added to dilute to the volume of the volumetric flask, to produce the analyte solution.

Draft Method 324, as performed by Frontier Geosciences, does not involve a filtration step; however, several of the participants did filter the acid extract and felt that it improved the mercury recovery.

The analyte solution is analyzed using an atomic fluorescence spectrometer with a gold amalgamator system for preconcentrating mercury during the analysis. High dilutions of the extract solution (100 times or more) are desirable to minimize chemical interferences in the solutions. Working standards for the analysis cover the range from 0.10 ng/mL (ppb) to 10 ng/mL mercury.

Draft Modified ASTM Method D 6414 – Acid Extraction/AAS or AFS

This method is a very extensive modification of Method ASTM D 6414 – Standard Test Methods for Total Mercury in Coal and Coal Combustion Residues by Acid Extraction/Atomic Absorption Spectroscopy (2). ASTM D 6414 is available from ASTM (www.astm.org) . Modifications were required to adapt this method to iodized activated carbon analysis. The new procedures developed during the project constitute a method quite different from ASTM D 6414. These procedures are outlined in Appendix A.3. EPRI's modification of D 6414 has not been submitted to ASTM for approval and has not been verified outside of this study.

In this draft method, the solid sorbent material is extracted in a hot concentrated nitric/hydrochloric acid mixture, the solution filtered and diluted with acid solution before analysis by atomic AAS or AFS. Highlights of the analytical procedure are as follows:

- A mixture of concentrated HNO_3 and concentrated HCl (aqua regia) is added to a digestion bottle and sealed with a cap.
- The mixture is heated for 1 hour in a 80°C water bath.
- The bottle is allowed to cool, opened, and 5 mL of 5% potassium permanganate ($KMnO_4$) is added, the bottle capped, the solution mixed thoroughly and allowed to stand for 10 min.
- A 0.5 mL portion of hydroxylamine sodium chloride solution is added and mixed. This is repeated until the pink color of $KMnO_4$ is gone.
- The total volume of analyte solution is about 50 mL; the volume is recorded for calculations.

Over the course of the project, it became apparent that procedures using higher acid strengths yielded better results. The additional acid strength is needed to release more mercury from the iodide-treated activated carbon during the extraction process. Once the carbon residue was filtered from the extract solution, the acid strength was not an issue. The acid mixture that works best is 30 mL of a 50:50 $HCl:HNO_3$ mixture added to the entire mass of sorbent material, yielding a final volume of 50 mL before filtering.

The analyte solution is analyzed using AAS or AFS. Dilutions of the extract solution are essential to minimize chemical interferences in the solutions. Working standards for the analysis cover the range 0.50 ng/mL (ppb) to 10.0 ng/mL mercury.

Thermal Desorption

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 RA-915 Mercury Analyzer. A summary of important considerations in applying the thermal desorption method to sorbent tube mercury analysis is given in Appendix A.4. Some details of the procedure are as follows.

- 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.
- The mercury is determined by AAS, with Zeeman correction. The signal is integrated over time, giving a measure of the total mercury produced during the analysis.
- The instrument must be calibrated with the same type of material as that being analyzed. In this instance, a mercury solution spiked onto the same iodized activated carbon as contained in the samples is used as the calibrant when analyzing the promoted activated carbon samples.

Direct Combustion Analysis/AAS

The full title of this method is ASTM D 6722 – Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis and Atomic Absorption Spectroscopy (3). The method is available from ASTM. The modification developed for this project is the homogenation of the solid sorbent material using a SPEX 8000M Ball Mill. The homogenized material is then analyzed using ASTM Standard Test Method D 6722, following the same procedure used for coal and coal combustion residues. During analysis, a 0.1 g sample of homogeneous solid sorbent material is first weighed into a nickel boat and analyzed with a LECO AMA 254 Mercury Analyzer. There are other vendors of direct combustion instruments, but only one model was tested in this study. Instructions for homogenization and analysis of the iodine-treated activated carbon sorbent material are given in Appendix A.5. Some details of the analysis procedure follow:

- The sample is dried by heating in oxygen at 100-120°C.
- The dry sample is heated to 750°C in oxygen.
- The combustion gases are passed over a catalyst heated at 550°C, which scavenges acid gases and condensing materials.
- Mercury in the combustion gases is captured on an amalgamator (gold coated ceramic).

- The amalgamator is heated to 900°C, which quantitatively releases the amalgamated mercury into the vapor phase for analysis by AAS.

Instrumentation

The types of analytical instrument used for the analysis of mercury in the acid extracts Phase I and Phase II of the project included the following:

- Flow injection AAS systems with reaction chambers, in which the mercury concentration is determined by the mercury released and measured constantly during the steady state operation of the system. This study included flow injection instruments from the following manufacturers:
    - Teledyne-Leeman
    - Perkin-Elmer Flow Injection Mercury System (FIMS)
    - CETAC Technologies
- Flow injection CVAAS system with a fixed reduction cell to which specific amounts of test solution and reducing solutions are mixed. All the mercury vapor produced during the analysis is measured by measuring total absorbance vs. time and the total signal integrated. The system used in this study was from Nippon Instruments
- Cold vapor/gold amalgamation with atomic fluorescence spectroscopy. The systems used in this project included instruments from the following vendors:
    - Tekran
    - Teledyne-Leeman

- Thermal Desorption/AA with Zeeman Correction. An Ohio Lumex RP-M324 Thermal Decomposition Furnace attached to a RA-915 Mercury Analyzer was used.

- Direct Combustion/AA (ASTM D 6722). A LECO AMA 254 Mercury Analyzer was used.

Study Coordination

In Phase I, study participants were not told the verified spike concentrations until after they had attempted several analyses. However, they were then notified of the concentrations, so that they would have immediate feedback on their results.

In Phase II, concentrations were not revealed to most participants until after all data was delivered to the study coordinator. However, it was necessary to reveal the approximate concentrations to Ohio Lumex users, as they are unable to repeat analyses and so had to know the appropriate calibration range in advance.

Instructions to the participants for preparing the QC samples are included in Appendix A.6.

3

PHASE I: FAMILIARIZATION

Phase I was used by participating laboratories to work out problems with selected analytical methods and equipment and to experiment with varying method conditions to improve recoveries of mercury from the spiked samples. This phase of the project also included evaluation and improvement of the spiking apparatus.

3.1 Spike Verification Analysis

Table 3-1 summarizes the results of the Phase I spike verification tests. Samples were analyzed by ARCADIS using thermal desorption and by Frontier Geosciences using Draft Method 324. Each lab analyzed 15 samples from the first batch of Phase I spikes (five samples each of three spike levels). The second batch of nine9 Phase I samples (three samples at three spike levels) were analyzed only by ARCADIS. The values reported for Phase I are listed in Appendix B.1.

The Phase I spike verification analyses determined that the spiked samples did not contain as much mercury as expected (300, 3000, and 10,000 ng), but instead contained between 74% and 85% of the planned spike. The difference was not due to poor analytical recovery of the spike: both confirmation laboratories detected similar low levels. ARCADIS attributed the low levels to incomplete transfer from the mercury solution to the gas stream, due to the design of the bubbler stem and non-optimal stannous chloride concentration. The lowest spike level had the highest percent transfer, indicating that the surface area of bubbles contacting the mercury solution was a limiting factor in the transfer of mercury from solution.

EPRI decided to proceed with Phase I using these samples, even though the mass of mercury on the samples was not as planned. The samples were still useful for evaluating the various test methods.

Both verification laboratories achieved good within-lab precision. The average percent relative standard deviation (% RSD) for Frontier Geosciences is 5.1% and 4.6% for ARCADIS. This precision was deemed acceptable for the overall spiking process, meeting EPRI's criterion for acceptance of spiked samples of 5 % relative standard deviation above the analytical method variability. It is impossible to separate the random errors inherent in the spiking procedure, or those from the analytical procedures, from the overall precision in the measurements.

Table 3-1
Summary of Phase I Verification Analyses

Nominal Spike (ng)	Actual Spike (ng)*	Thermal Desorption			Draft Method 324			Ratio TD/324
		Average (ng)	% Recovery	% RSD	Average (ng)	% Recovery	% RSD	
Batch 1								
300	296	244	82	5.2	253	85	5.7	0.96
3,000	2932	2226	76	6.9	2330	79	6.4	0.96
10,000	9982	7608	76	1.7	7586	85	3.2	1.0
Batch 2								
300	296	247	83	4.9	–	–	–	–
3,000	2932	2547	87	1.9	–	–	–	–
10,000	9982	7757	78	1.5	–	–	–	–

* Spike corrected for volume of mercury standard solution added

3.2 Stability Evaluation

A set of Phase I sample tubes was reserved for stability testing. The tubes were stored under refrigeration in sealed plastic bags. One year after the samples were prepared, they were analyzed by ARCADIS using the thermal desorption method. Data from the August 2005 analysis of five samples of each spike level and from the August 2006 analysis (eight samples of the low and medium spike levels and four of the high spike level) are given in Table 3-2. The average % recovery was unchanged, which indicates the spiked samples are apparently stable over a one-year period. The differences between the averages obtained for each spike level are much smaller than the variability of either the sample preparation or the sample analysis. The decrease in the % RSDs in August 2006 compared to those in August 2005 further indicate the improvement in the precision of the thermal desorption results over the project period, as noted above.

Table 3-2
Stability of Phase I Samples

	August 2005			August 2006		
	Low	Medium	High	Low	Medium	High
Desired Loading (ng)	300	3,000	10,000	300	3,000	10,000
Average (ng)	244	2226	7608	246	2272	7587
% Recovery	82	76	76	82	76	76
Average % Recovery		78			78	
% RSD	5.2	6.9	1.7	3.9	4.3	1.3

3.3 Laboratory Setup and Method Evaluation

The Phase I period was used by the participants to set up their labs and learn the procedures. At the beginning of this project, only one laboratory was set up to follow one of the procedures, and this lab did not participate in Phase I. None of the other labs had extensive experience in analyzing the iodide-treated activated tubes that were used in the project. Some of the labs lacked proper instrumentation. A considerable amount of effort was expended by the labs to properly equip their labs, and to work out details of adapting their chosen procedure.

At the beginning of Phase I some of the participants' perceived problems with sorbent tube analysis were:

- Limited or no experience in performing the extractions and/or analyses.
- Suitability of analytical instrumentation for the analysis.
- Finding suitable clean laboratory space.

During Phase I the project study coordinator worked with the participants to address the above problems, including visiting most of the laboratories, reviewing their procedures, and evaluating their equipment and laboratory setup. All of the participating labs were judged to have personnel with training sufficient to perform the extractions and/or analysis, adequate instrumentation to carry out the proposed methods, and available clean laboratory space to carry out the procedures they intended to use during the project.

For the Modified ASTM Method D 6414 extraction method each participating laboratory had to adapt the method they chose to use to their own laboratory and the mercury analysis instrument they had in their laboratory. The spiked samples distributed during Phase I allowed the individual laboratories to experiment with several different acid mixtures, extraction vessels, heating blocks or baths, etc. Some combinations of reagents and procedures clearly did not produce acceptable recoveries of mercury from the carbon, while others appeared to be acceptable. Following is a list of the types of materials and equipment used to produce acceptable results during Phase I.

<u>Modified Method D 6414</u>

- The extraction acids used were either aqua regia or 50:50 hydrochloric:nitric acids.
- The sequence of adding acids were to add HCl first to minimize formation of nitrogen oxides.
- The extraction vessels and heating systems used were glass BOD or polycarbonate bottles in a water bath, or Thermal Express plasticware in a heating block. All vessels must have tight fitting lids capable of withstanding the pressures during heating.

Proper heating of the extract mixture was found to be very important. Trials by the various labs showed that heating the extraction vessels at temperatures below those prescribed in the procedures gave low results, while heating at temperatures higher than those prescribed sometimes gave less than the expected results. It was speculated that some of the solution and mercury was lost during heating at the higher temperatures.

One commonly used step in the extraction procedures that was found to have a significant impact on results is the filtering of the extraction solution. Some labs used conventional ashless filter paper and filtering funnels while others used syringes with fitted PTFE filters to separate the suspended materials from the extract solution. The concentrated extract solutions were filtered, before dilution, to minimize readsorption of mercury in the carbon-based sorbent material.

Draft Method 324, as performed by Frontier Geosciences, does not include a filtering step, but two laboratories that chose to use this method found that filtering the carbon residue from the extract solution as soon as possible after the extraction step improved mercury recovery. Both of these labs filtered the extracts before diluting with the bromine chloride solution.

The filtered extract solutions appeared to be stable for several weeks. Some of the labs stored the extracts in refrigerators and checked the analysis weeks later to find no significant changes in the concentrations.

As the project proceeded, it became apparent the major analytical challenge in the entire project was interference of iodine in the calibration and analysis procedures. The source of the iodine causing the interference is the iodide-treated activated carbon used as the sorbent material. During the extraction and analysis processes the following reactions may occur.

$$2NO_3^- + 8H^+ + 6I^- \bullet 2NO(g) + 4\,H_2O + 3I_2(s)$$

The standard electrode potential (E_{Rxn}^{o}) for this reaction is 0.424 volts, which means this is a spontaneous reaction. The iodide and nitrate ion are not compatible in acid solutions. In solution the iodide ion and molecular iodine form the colorless I_3^- ion. When stannous chloride is added to the solution during the analysis stage, the stannous ion and I_3^- react as illustrated by the following equations.

$$I_2(s) + I^- \bullet I_3^-$$

$$I_3^- + Sn^{2+} \bullet 3I^- + Sn^{4+}$$

The standard electrode potential for the latter reaction is 0.396 volts, which means it is a spontaneous reaction. The desired reaction between stannous chloride and the mercuric ion is shown in the following equation:

$$Hg^{2+} + Sn^{2+} \bullet Hg^0 + Sn^{4+} \text{ (in solutions with HCl)}$$

The desired reaction has a standard electrode potential of 0.309 volts, which means that it is less favored than the previous reaction between I_3^- and stannous chloride acid solution. Also, mercuric ion reduction is less favored in solutions with iodide ion, because of the lower solubility of HgI_2, which lowers the standard electrode potential for mercuric ion reduction.

The molecular iodine problem is an example of chemical interference, since the iodine reacts with species other than the analyte and interferes with the reduction of mercury, the analyte. This type of interference is much more difficult to deal with than more common matrix interferences. The preferred solution to the problem is to somehow remove the molecular iodine from solution; however, this is almost impossible, since the acidic character of the solutions must be kept very high. Attempts to extract the molecular iodine with organic solvents removed a considerable amount of the mercury as well.

Experiences of the participating Phase I labs showed that the only known way to minimize the molecular iodine interference is to dilute the extract solutions as much as possible. Although this does not remove the effect molecular iodine has on the analysis of mercury in the diluted solution, the effect is minimized to the point that reproducible results could be obtained.

3.4 Phase I Results

The Phase I data submitted by the participating laboratories are summarized in Table 3-1, and are listed in Appendix B.1. The two sets of data at the top of the list are the spike verification results for the first batch of Phase I samples. These values established the "accepted" concentrations of mercury in the sorbent tubes. Five labs submitted data from the first batch of samples and two labs submitted data from the second batch.

Some labs submitted data for each of the 30 samples, while some submitted data for just a few samples. Over the course of the study, these data show the progress of the labs in developing and improving their labs and the analytical procedures. In general, the data show a gradual improvement in the results in going from the top (initial runs) to the bottom (final runs) for each lab.

The spike level that generated the most problems for the labs using the two acid extraction procedures was the lowest spike level (~300 ng). The most likely reason for this difficulty was the interference of molecular iodine in the analysis. The magnitude of the iodine problem was not realized early in the project, and early difficulties with the low spike level samples were attributed to lack of sensitivity of some of the mercury analysis systems being used by the labs. However, by the end of Phase I, it became clear that the most prominent problem for labs using the extraction method and AFS/AAS procedures was the molecular iodine interference.

The data from the Phase I results were not intended for statistical evaluation, as the primary purpose of this phase was laboratory familiarization with the methods. However, it was still desirable to compare the precision of the different methods, to evaluate the likelihood that the test methods selected by participants could be used in an expanded round robin to generate data similar to that needed for establishing a standard method.

Phase I data were evaluated using ASTM Practice E 691 – *Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method* (1). E 691 is used for the statistical evaluation of round robin data to prepare precision statements for ASTM standard methods.

A significant challenge in evaluating the Phase I data was that the laboratories changed sample preparation procedures frequently, as they improved their capability to analyze the samples and experienced some failures in their initial efforts. An effort was made to "salvage" sufficient data to evaluate the four methods. The data and reporting notes from each laboratory were carefully examined to exclude data from improperly run or failed analyses. These tests were relatively easy to identify from the laboratories' notes and/or data outliers. Following the removal of these numbers, the remaining data entries were grouped in ascending order of mercury level for each lab. The middle four entries for each spike level in each lab were then selected for E 691 calculations. Missing data from several labs restricted the calculations to four entries.

The seven laboratories contributing four or more analyses for each spike level included the two sample verification labs. One laboratory submitted data for the second set of Phase I samples. The mercury contents in the two sets of samples were not exactly the same, based on the verification analyses, so the data from the second set was converted to the first set basis using a ratio factor. This factor was calculated from analytical data supplied by ARCADIS, who analyzed multiple samples from each set as part of the verification study discussed above.

The data used in the E 691 calculations are given in Appendix B.1.1. All four test methods, identified as 324 (Draft EPA Method 324), TD (Thermal Decomposition), M6414 (Modified ASTM D 6414), and DC (Direct Combustion) are represented in the data set. Table 3-3 lists the precision parameters generated by E 691. The definition and/or meaning of the parameters are as follows.

- The **k column** shows the number of labs reporting a mercury measurement outside of the statistical range of the other data produced by that laboratory.
- The **h column** shows the number of labs reporting an average mercury concentration outside of the statistical range of the other data.
- The **"r"** value represents "in lab" *repeatability* at the 95% confidence level.
- The **"R"** value represents "between lab" *reproducibility* at the 95% confidence level.
- ***Sr*** is the pooled standard deviations for all replicates in each lab.
- ***SR*** is the pooled averages of standard deviations for the labs.
- ***Repeatability (r)*** is the value below which the absolute difference between two test results of separate and consecutive test determinations, carried out on the same sample in the same laboratory by the same operator using the same apparatus on samples taken at random from a single quantity of homogeneous material, may be expected to occur with a probability of approximately 95%.
- ***Reproducibility (R)*** is the value below which the absolute difference between two test results, carried out in different laboratories using samples taken at random from a single quantity of material that is as nearly homogeneous as possible, may be expected to occur with a probability of approximately 95%.

The information in Table 3-3 indicates there is not a wide variability in the selected data, since there are only two out of 21 possibilities for k (seven labs x three spike levels) that show an in-lab precision outside the selected statistical range for the three spike levels. The h values show there is one lab with between-lab precision outside the selected range. Sr and Sr are multiplied by 2.8 to convert to the 95% confidence levels.

Table 3-3
Statistical Parameters for Phase I Samples Calculated by ASTM E 691

Labs	Average	Sr	SR	Suspect k	Suspect h	r	R
7	254.0	19.2	43.2	1	0	54	121
7	2423.4	139.6	164.6	0	0	391	461
7	7483.8	385.31	605.8	1	1	1079	1696

Table 3-4 compares E 691 repeatability and reproducibility statistics from the Phase I data with the statistics for the published ASTM standard method D 6414 (2), used for the analysis of mercury in coal and combustion residues. The applicable concentration range is wider for sorbent tube samples, although the D 6414 standard method is applicable at a lower concentration (32 ppb).

Comparing the linear equations representing the repeatability for the methods, the slope for the sorbent tube data is a little higher (0.141 for sorbent tubes vs. 0.11 for D 6414). This indicates there is higher variability (lower precision) in the activated carbon measurements compared to that for D 6414. For reproducibility, the slope of the equation for the Phase I data is lower (0.223 vs. 0.25 for D 6414). This indicates the between-lab precision for the carbon tube measurements is better than that obtained in the D 6414 method verification study. These comparisons were very encouraging, since the carbon tube data were obtained using four separate methods and instrumental techniques in various stages of development, compared to D 6414, which uses two extraction procedures and one instrumental method (AAS).

Table 3-4
Comparison of Phase I Estimated Repeatability and Reproducibility Intervals with ASTM D 6414

Method	Concentration Ranges	Repeatability, r	Reproducibility, R
Phase 1 data	254-7584 ng/tube section = 127-3800 ppb	Y = 0.141x + 31.3	Y = 0.223x + 5.74
D 6414 (for coal)	0.032-0.585 ppm = 32-585 ppb	Y = 0.11x + 0.012	Y = 0.25x + 0.003

Where x = average of 2 successive analyses

3.5 Suggestions for Phase II

Based on the Phase I results, the primary problems with analysis of the Appendix K sorbent tubes appeared to be related to the acid digestion procedures, in particular the ratios of different acids used in the Modified D 6414 analysis. All participants were cautioned to follow the procedures and guidelines as closely as possible, especially the acid digestion procedures. All participating laboratories were asked to establish a plan for analysis of the samples so that the entire set would be completed in no less than three batches. Quality control samples, prepared by adding a weighed amount of the NIST SRM 1641d to the blank iodide-treated carbon material, were included as the best available approximation of a sorbent tube spiked with a certified value of mercury. The QC samples were used to check for any bias(es) in the analytical procedures used in the study.

A procedure was suggested for reducing the extent of the molecular iodine interference. The suggested approach was to use a variation of the well-known analytical procedure of standard additions. The suggested variation is appropriately called the “sample addition” method. A specific set of instructions on how and when to use the sample addition procedure was prepared and sent to all participating labs at the beginning of Phase II. The use of this procedure was voluntary, as it required additional laboratory effort in preparing sequential additions of each spike level. A copy of these instructions is given in Appendix A.6.

4

PHASE II: MULTILABORATORY STUDY

The purpose of Phase II was to evaluate the performance of various test methods, as well as to give participating laboratories a metric to evaluate their own performance. For this part of the project, participants were provided samples of unknown concentration and were not supplied the verified spike values until after all data were reported.

4.1 Spike Preparation and Verification Analysis

As discussed in Section 2, a modified spiking apparatus was used to produce the Phase II samples. Before the samples were prepared, ARCADIS conducted an internal study (funded by the EPA) to verify their ability to obtain quantitative transfer of mercury to the sorbent tubes using the modified apparatus. As part of that study, ARCADIS analyzed samples in-house by thermal desorption analysis and also submitted samples to Frontier Geosciences for analysis by Draft Method 324. Table 4-1 lists the results of these analyses. Each laboratory analyzed six samples at each of four spike levels, ranging from 50 ng to 20,000 ng/tube section.

The thermal desorption results indicated 94-104% transfer, based on the ratio of measured to spiked mercury, but the Draft Method 324 results showed lower apparent transfer. The ratios of the thermal desorption/Draft 324 results ranged from 1.05 to 1.2 for the four levels. The source of this discrepancy could not be determined from the data: possible explanations include low recovery in the acid digestion procedure or interferences or calibration errors in the analyses from one or both of the laboratories. The spike concentrations were known in advance to ARCADIS, but were not known by Frontier Geosciences.

The precision of the combined spiking and analytical procedures appears to be better than for Phase I, with a % RSD ranging from 1.9 to 3.9% for ARCADIS, and 1.5 to 3.8% for Frontier Geosciences. The average % RSD is 2.9% for ARCADIS and 2.7% for Frontier Geosciences. These %RSDs likely indicate improvement in the spiking precision, since the majority of the effort to improve the overall process were targeted at the spiking procedure. The precision of the analytical procedures may have improved as well.

Table 4-1
Results of ARCADIS Internal Study of Modified Spiking Apparatus

Spike Level (ng)	Thermal Desorption			Draft Method 324			Ratio TD/324
	Average	% Recovery	% RSD	Average	% Recovery	% RSD	
50	50	104	3.9	42	87	3.8	1.2
200	194	100	1.9	168	89	2.5	1.15
2,000	1,844	94	2.7	1,750	90	2.8	1.05
20,000	19,808	99	3.1	1,732	90	1.5	1.12

The modified apparatus was judged acceptable for preparation of the Phase II spikes based on the precision of spiking. Table 4-2 shows the nominal and actual spike levels from Phase II, along with the average measured concentrations, percent relative standard deviations, and recovery ratios for the Phase II spike verification samples. The verification samples were analyzed by the same laboratories and by the same methods as in Phase I. The spike levels were known to ARCADIS, but were blind to Frontier Geosciences. Each verification laboratory analyzed five samples at each of the six spike levels, the same number of replicates used in the round robin.

The average % RSD for the thermal desorption data is 1.75%, which is lower than the two previous sets (4.6% and 2.9%) of data from this lab. The average % RSD for the Draft Method 324 data is 5.4%, which is higher than the two previous set of data (5.1% and 2.7%) for this lab. One factor contributing to this higher % RSD is likely the lower spike level of 39.9 ng, for which this lab reported a % RSD of 14%. The average % RSD for the lab without this spike level is 3.6%. The ratios of the thermal desorption/Draft Method 324 data for the two labs are higher for the Phase II samples than for the ARCADIS internal spiking study, an average of 1.16 for all samples.

Table 4-2
Summary of Phase II Verification Analyses

Nominal Spike (ng)	Actual Spike (ng)*	Thermal Desorption			Draft Method 324			Ratio
		Average (ng)	% Recovery	% RSD	Average (ng)	% Recovery	% RSD	TD/324
40	39.9	38.8	97	2.2	32	80	14	1.22
250	249	249	100	2.3	203	81	6.9	1.23
2,500	2,491	2,492	100	1.3	2,069	83	4.2	1.20
9,000	8,977	9,015	100	1.4	7,848	87	1.6	1.15
25,000	24,910	25,001	100	1.9	22,929	92	3.2	1.09
40,000	39,856	39,104	98	1.4	36,131	85	2.0	1.08

* Spike corrected for volume of mercury standard solution added

Some statements can be made about the spike verification results shown in Tables 4-1 and 4-2, compared with the Phase I verification results shown in Table 3-1 .

- The precision of the spiking procedure improved during the course of the project, as measured by the percent relative standard deviations of the analysis of the spiked samples.
- The precision of the mercury measurements using the Thermal Desorption Method (Ohio Lumex) apparently improved during the course of the project. The total precision is the combination of the spiking procedure precision and the analytical measurements precision.

- The progressively better precision in the three sets of thermal desorption data, as measured by the decrease in % RSDs (4.6% to 2.9% to 1.75%) can not all be attributed to the increasing precision of the spiking procedure. Some of it is due to the improvement in the mercury measurements.
- There was an increase in the ratios of mercury values measured by thermal desorption and Draft Method 324 between the Phase I spike verification (average ratio = 0.97) and the ARCADIS internal study (average ratio = 1.13). This difference persisted in the Phase II spike verification (average ratio = 1.16). The change in ratios was due to the thermal desorption method measuring values closer to the target spike level, while the Draft Method 324 values continued to measure concentrations of about 80-90% of the target spike level. Further investigation is required to determine the reason for this discrepancy.

4.2 Data Summary

The eleven sets of results submitted for the Phase II samples are listed in Appendix B.2. The results were submitted without any corrections for blanks or for the spike recovery indicated by the quality control sample. All submitted reports were carefully checked for reporting errors, and discrepancies were checked with the participating labs. Three outlier data points were identified in the 330 reported values (11 data sets x 30 samples) and were dropped. The difference between each outlier and the closest retained value was more than 4 standard deviations. After dropping the outliers, all data sets were corrected (if needed) for reagent blanks. Concentrations were not corrected for sorbent tube blanks, as blank correction is not permitted in Appendix K. The corrected data are given in Appendix B.2.1.

Summaries of laboratory averages, percent recoveries, standard deviations, and percent relative standard deviations for the corrected data are given in Table 4-3. Using the summaries in the table, charts were prepared to help evaluate the data and to better illustrate any differences between methods. The statistics used to prepare these charts are presented in Appendix B.2.2.

Figure 4-1 shows the average % recoveries and % RSDs for the six spike levels used in Phase II. The data are shown grouped by analytical method. All of the data sets except TD-1 are from analysis of blind samples (concentration not known to the laboratory).

Figure 4-2 shows the average % RSD for the six spike levels and the average % RSDs for the four sets of results closest to the theoretical spike level. As shown in Table 4-3, the % RSDs are considerably higher for the 40 ng spike level than for the other spike levels. This pattern also held true for the four labs that reported results closest to the actual spike level, indicating that even the best performing labs had difficulty in obtaining precise measurements at the 40 ng level. The increase in %RSD at low concentration generally indicates that a method may be operating beyond its working range.

Table 4-3
Summary of Phase II Results by Laboratory

Nominal Spike (ng)	Actual Spike (ng)[1]	TD-1[2,3]	TD-2	DC	324-1[2]	324-2	324-3	M6414-1	M6414-2	M6414-3	M6414-4	M6414-5
		Laboratory Average (ng)										
40	40	39	29	27	32	37	39	18	20	37	ND	40
250	249	250	243	238	203	220	284	132	141	204	ND	246
2500	2491	2492	2300	2618	2069	2218	2675	1271	1432	1826	1616	2433
9000	8968	9015	8364	9188	7848	8889	9183	6578	5475	7002	6477	8705
25000	24910	25001	20200	25346	22930	23674	25396	18268	11960	22713	16871	23783
40000	39856	39104	32320	39038	36131	39791	37447	27980	18430	37613	31393	38615
		% Recovery										
	40	97	74	66	80	93	97	44	50	92		99
	249	100	98	96	81	88	114	53	57	82		99
	2491	100	92	105	83	89	107	51	58	73	65	98
	8968	101	93	103	88	99	102	73	61	78	72	97
	24910	100	81	102	92	95	102	73	48	91	68	96
	39856	98	81	98	91	100	94	70	46	94	79	97
		Standard deviation (ng)										
	40	0.84	3.5	2.8	4.6	4.7	22	2.9	4.8	3.2		8.8
	249	5.8	5.6	8.3	14	4.0	52	8.4	6.5	14		2.3
	2491	31	64	37	87	36	383	65	53	93	267	40
	8968	130	159	96	124	686	715	898	187	617	338	69
	24910	471	967	392	739	547	1684	2470	552	3627	2430	130
	39856	566	1195	398	707	1267	1264	2238	623	7018	1362	147
		% Relative standard deviation										
	40	2.2	11.9	10	14	13	58	17	24	8.7		22
	249	2.3	2.3	3.5	6.9	1.8	18	6.3	4.6	6.7		0.93
	2491	1.3	2.8	1.4	4.2	1.6	14	5.1	3.7	5.1	17	1.6
	8968	1.4	1.9	1.0	1.6	7.7	7.8	14	3.4	8.8	5.2	0.79
	24910	1.9	4.8	1.6	3.2	2.3	6.6	14	4.6	16.0	14.4	0.54
	39856	1.5	3.7	1.0	2.0	3.2	3.4	8.0	3.4	18.7	4.3	0.38

ND – not detected, [1] Spike corrected for volume of mercury standard solution, [2] Verification laboratories, [3]Spike was not blind to laboratory

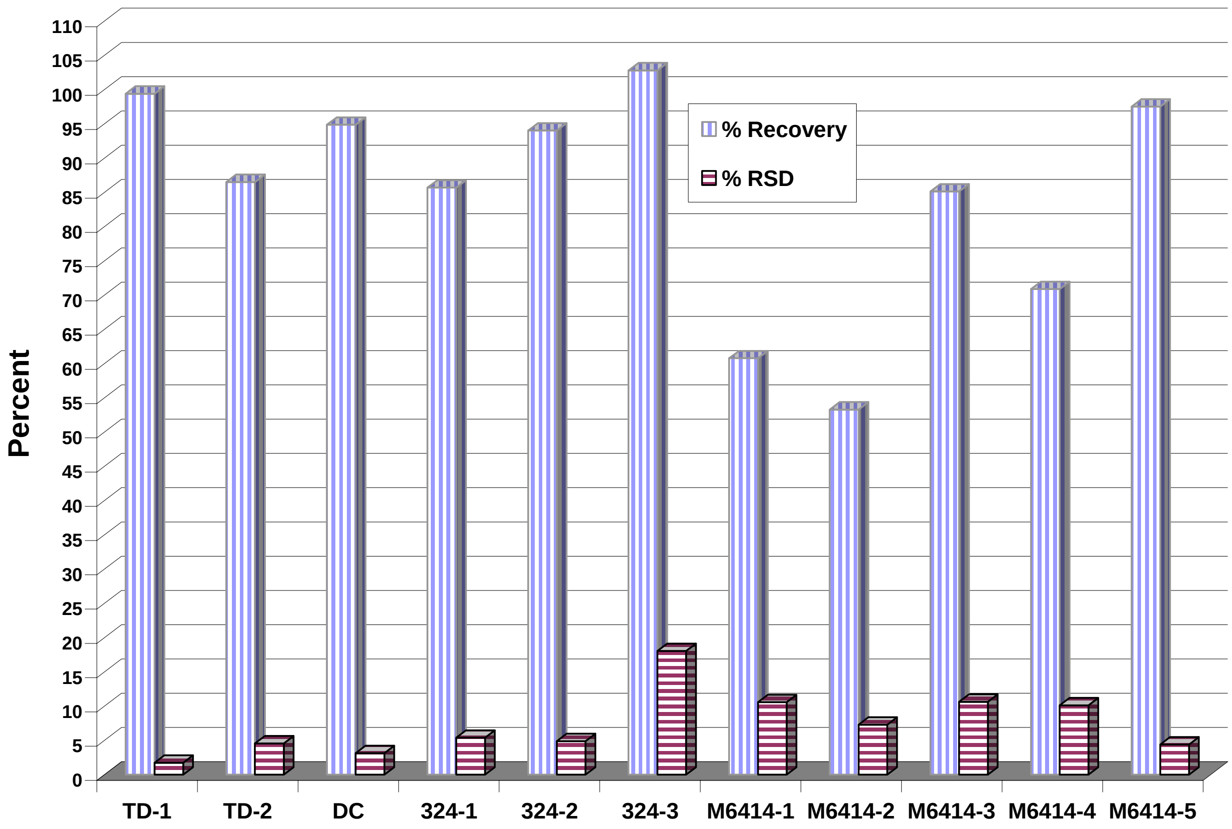

Figure 4-1
Average % Recoveries and % RSDs for All Six Spike Levels

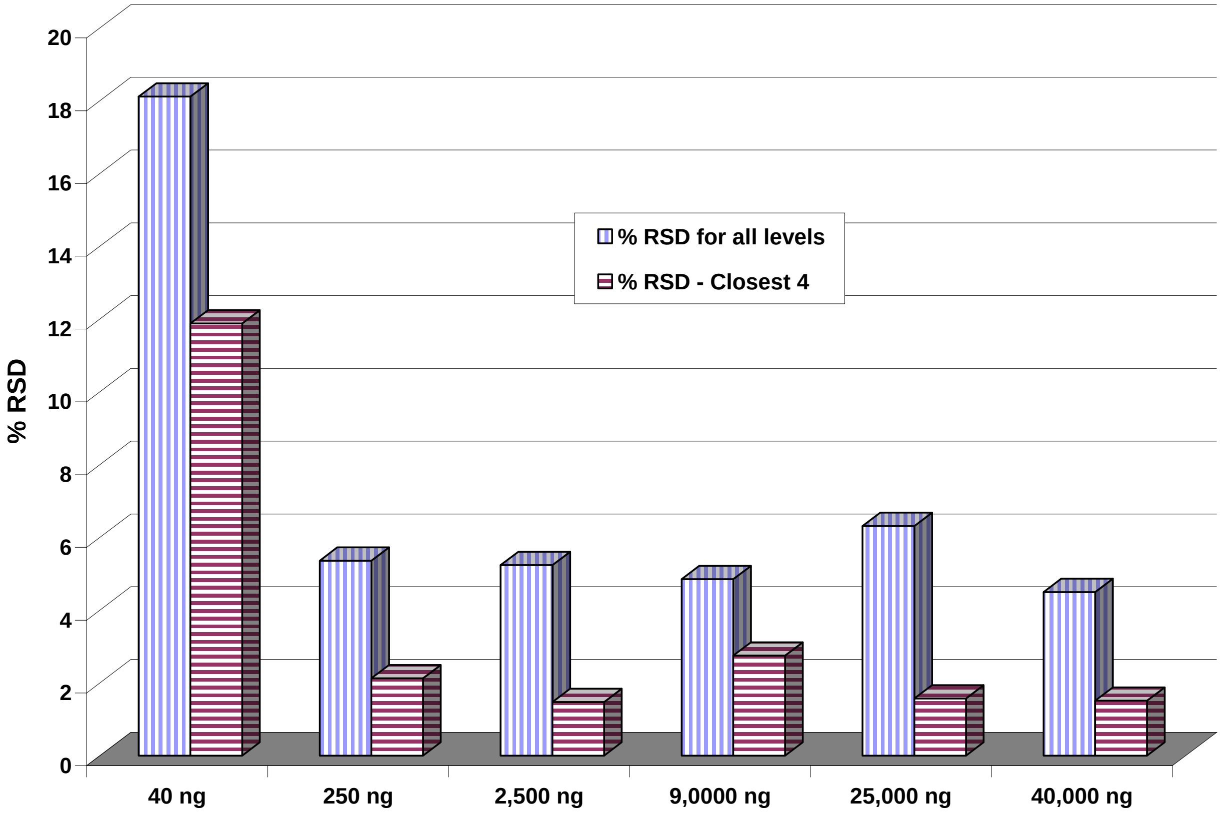

Figure 4-2
Average % RSDs for Four Labs Closest to the Theoretical Spike Level

4.3 Evaluation of Phase II Results

The 11 data sets contain two sets using thermal desorption (TD), one set using direct combustion (DC), 3 sets using Draft EPA 324 Method (324), and 5 sets using Modified D 6414 Method (M6414). The volumes and blends of acids used in the M6414 analyses varied among laboratories. All except the TD-1 set are blind analyses.

Three criteria were used to assist in the data evaluation:

- Use of t-statistics at the 95% Confidence Level
- Use of ASTM Practice E-691 (95% Confidence Level)
- Appendix K Criteria of 85-115% Recovery at three Spike Levels

A matched pair "t statistics" calculation was performed to determine whether or not there is a significant difference between the data reported for the 40 ng spike level and the other five spike levels. The calculations show there was a significant difference between these two sets of data at the 95% confidence level (4). Further statistical evaluations were carried out without the 40 ng spike level sample. Figure 4-3 shows the percent recoveries for the five highest spike levels and the % RSDs for both five and six levels. The figure shows there is a considerable difference between the variability in the five-level measurements and that of the six-level measurements.

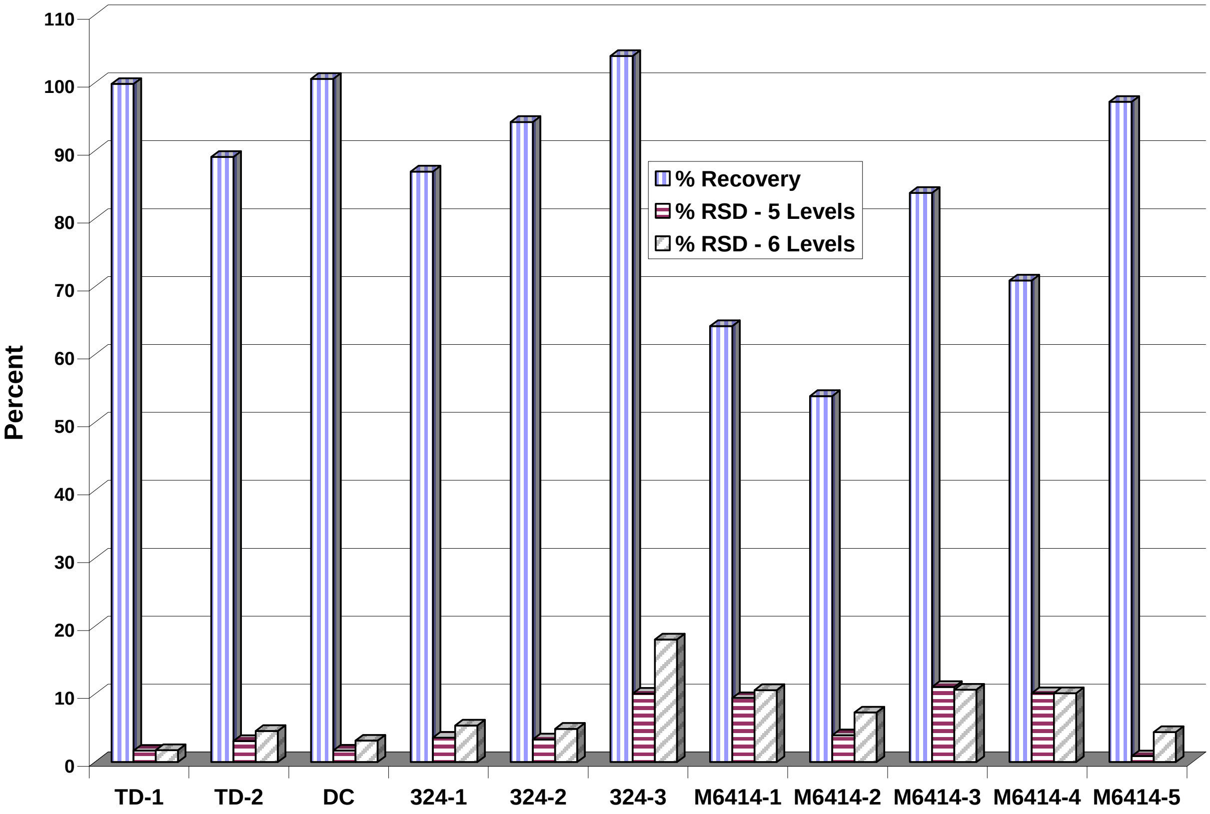

Figure 4-3
Average %Recoveries for Five Spike Levels, and %RSDs for Five and Six Spike Levels

Data submitted for the quality control samples was examined to see if there were any differences between the percent recoveries for this sample and other round robin samples. The two spike levels closest to the QC sample concentration were examined for comparison. Figure 4-4 shows the relative values of the percent recoveries for the QC sample and the average of the two closest spike levels. The chart shows that, in general, the largest differences between the QC sample percent recovery and that for the two closest spike levels were greatest for those labs with low overall recoveries.

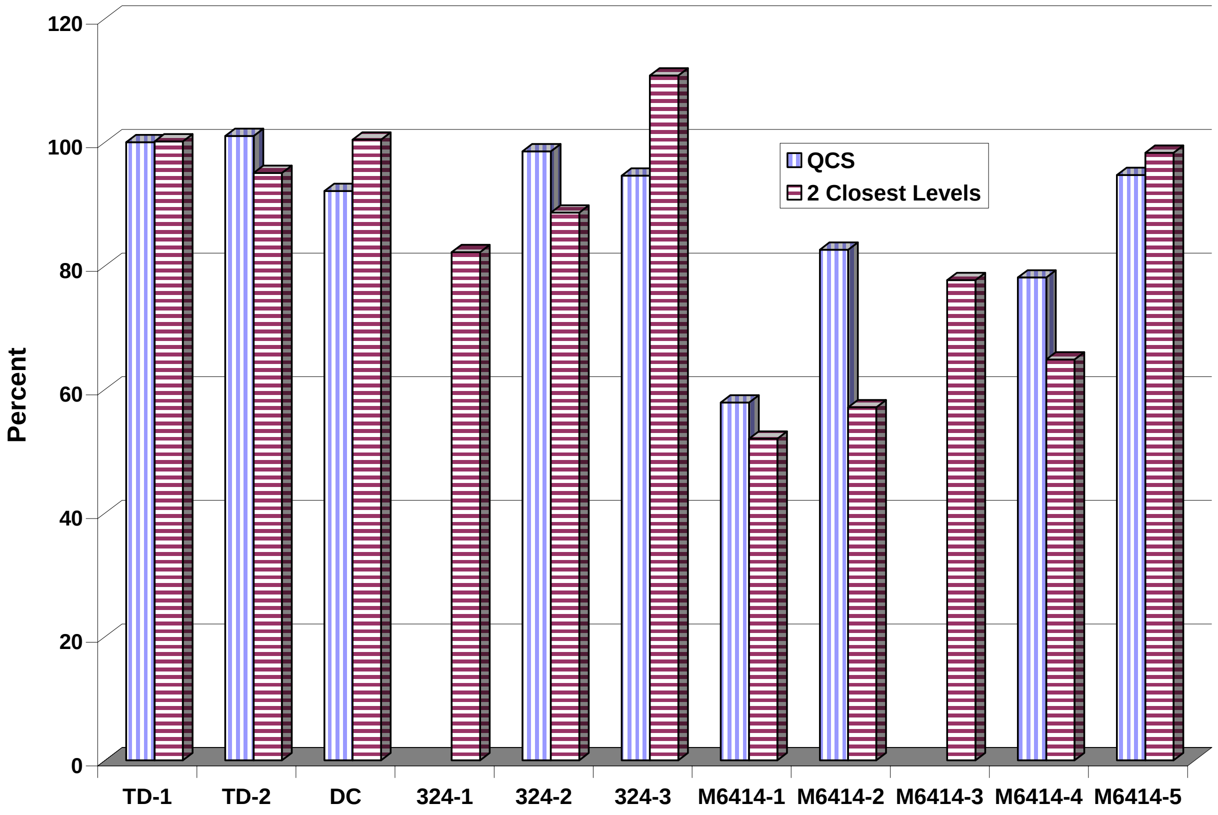

Figure 4-4
Average % Recoveries for the QC Sample and the Two Spike Levels Closest to It

Figure 4-5 is a plot of the average percent recoveries for the highest five spike levels, for each of the four methods. The average percent recoveries using M6414 are lower than those for the other three methods. The averages for the other three methods are about the same. The different levels of recoveries for the labs using the M6414 procedure are due to various factors, the more apparent being the molecular iodine interference followed by insufficient dilution and "borderline" analytical instrumentation. Both of these factors have been discussed previously.

An additional factor revealed by the round robin data was the overall acid strength needed for extraction of mercury from the sorbent material. In the round robin study, three labs used 16 mL of aqua regia, one used 12 mL and another 30 mL of $HCl:HNO_3$. Out of these five labs the one using the highest concentration of acid (30 mL of $HCl:HNO_3$) reported the highest recoveries and lowest % RSDs. One of the labs using aqua regia also reported acceptable recoveries, but did not have the dilution/instrumentation problems encountered by others. It is highly recommended that only the 30 mL of $HCl:HNO_3$ acid solution be used to extract the sorbent material, with a final extraction volume of 50 mL before filtering, when using the M6414 method.

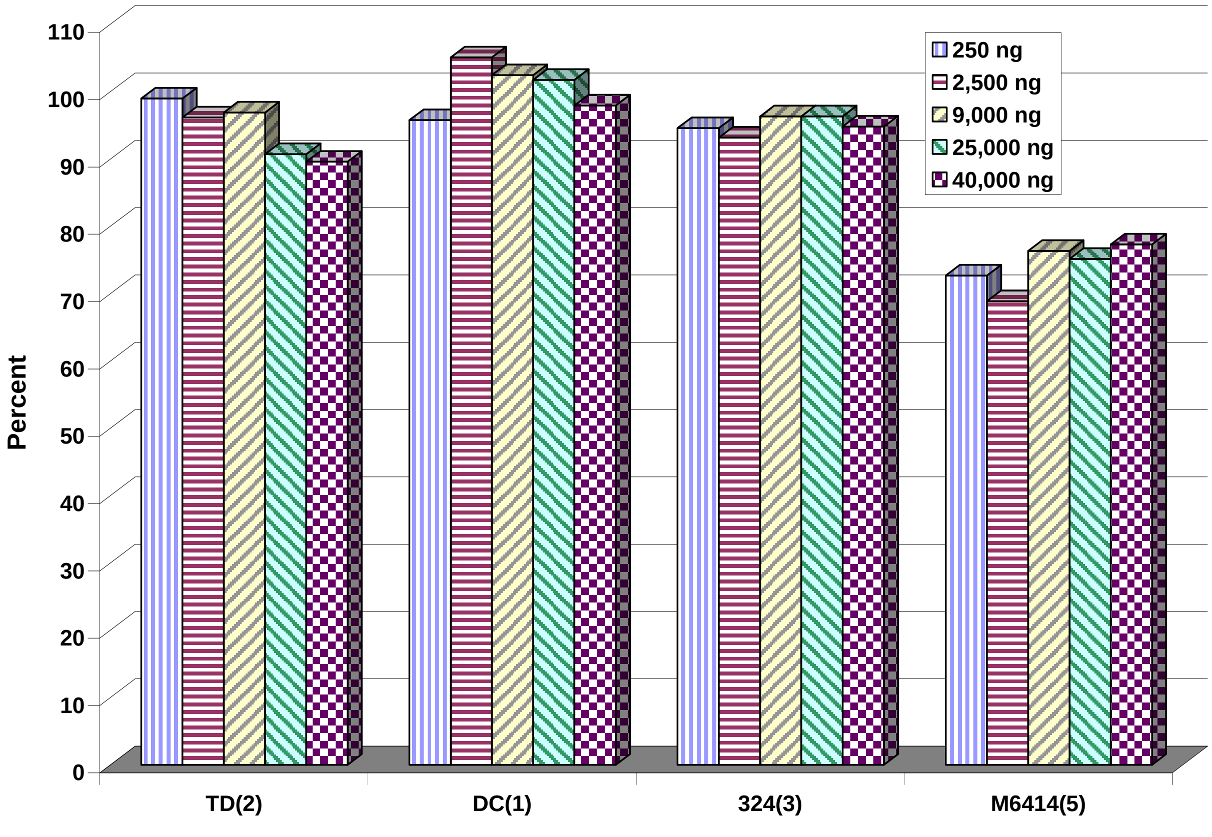

Figure 4-5
Average % Recoveries for Five Spike Levels, by Method (Number of Labs)

Since many of the laboratories involved in this study were still learning and optimizing the methods, it is appropriate to ask what is the best performance that can be expected from each of the four methods used in this study. The data sets with the lowest % RSDs and highest % recoveries were selected. Plots of the % recoveries for these four data sets are shown in Figure 4-6. Considering only the best-performing laboratories, one would be hard pressed to make a case for preference of one of the analytical methods over the other three. The similarity in the results was remarkable, considering the wide range of recoveries seen in Phase I.

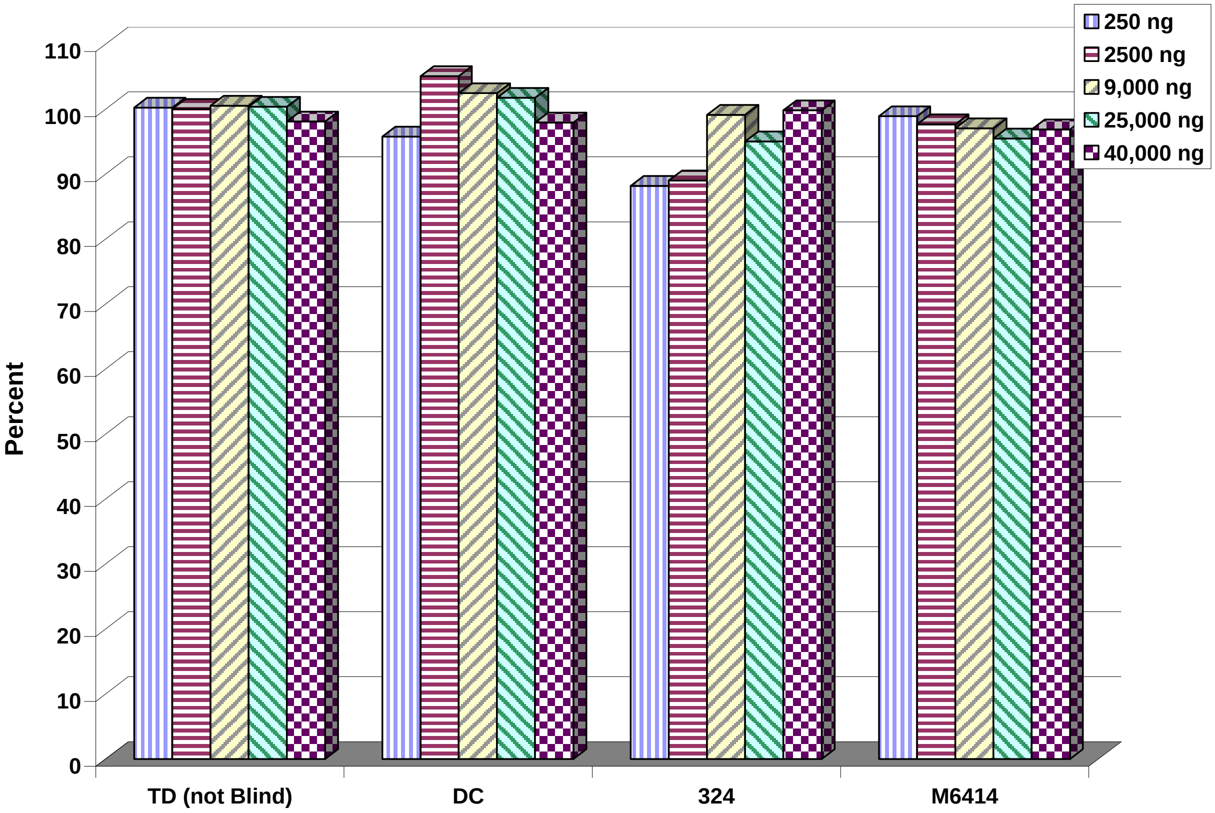

Figure 4-6
Average % Recoveries for Lab Results Closest to the Theoretical Spike Level

4.3.1 Evaluation of Method Precision by ASTM E 691

The 11 data sets from Phase II were included in an ASTM E 691 calculation, the results of which are shown in Table 4-4. The 40 ng sample was not included in the calculation, as discussed earlier in this section. The precision parameters, r and R, in Table 4-4 are much too high and not acceptable for a standard method. Most of the R values representing the between-lab precision calculated for this set of samples are over 50% of the average sample values. It should be noted that the data set used for the Phase I E 691 trial calculations was the best four, out of a possible ten runs, for each lab. The data in Table 4-4 are for all the data submitted in Phase II, with only the three outliers (out of 275 values) and the low 40 ng spike level samples removed. At this point there was no preselection of data sets, as was done for the trial E 691 calculation in Phase I.

Table 4-4
Statistical Parameters for Phase II Samples Calculated by ASTM E 691

Labs	Average (ng)	Sr	SR	Suspect k	Suspect h	r	R
11	216	18	51	1	0	51	142
11	2086	135	500	2	0	379	1401
11	7884	466	1363	1	0	1305	3818
11	21467	1572	4471	1	0	4402	12520
11	34334	2132	6767	1	1	5969	18946

It is to be emphasized at this point that there are too many unknown and uncertain variables contributing to the variability of the entire collection of data to make a recommendation that it be considered for a standard test method at this time. It should also be emphasized that the laboratories were still learning the methods and several had problems with procedures or instrumentation that were not resolved during the study. This does not mean that Appendix K methods are not suitable for development into a standard test method, it only means we did not make it to this level during the current study.

Assuming the round robin data could be subjected to a rigid statistical analysis for evaluation as the basis for a possible standard test method, there are some criteria that can be used to improve the overall data set. The following evaluation is simply an exercise to see how much the entire collection of data can be improved and how close it may come to acceptable precision intervals. There are three criteria that can be used to assist in the data evaluation.

- Use of t-statistics at the 95% Confidence Level
- Use of ASTM Practice E-691 (95% Confidence Level)
- EPA Criteria of 85-115% Recovery at Three Spike Levels

Applying matched pair t-statistics calculations, like those used for the spike level evaluations, to the 11 round robin data sets shows there are significant differences between the M6414-1 and M6414-4 data sets and the other nine sets at the 95% confidence level. This casts a level of uncertainty on these two data sets. Other factors to consider in examining this uncertainty are whether or not there were problems in the application of the analytical method and/or analytical instrumentation used in the analysis. In these cases there were such problems, including insufficient dilution to minimize the iodine interference and borderline instrumentation.

ASTM Practice E 691 has specific guidelines that can be considered in the evaluation of round robin data. Evaluation of the % RSDs from the six spike levels shows the average % RSD of the 40 ng spike level (18.1%) is more than three times the average % RSDs (5.25%) of the other five levels. This difference is sufficient cause to drop the 40 ng spike level from consideration for E 691 precision calculations. The same conclusion was reached using matched pair t-statistics calculations, as already discussed. Practice E 691 also allows a data set to be ignored in the calculations of precision if the set has missing data for one or more samples. The data set 6414-4 does have missing data, primarily due to the lack of sensitivity of the analytical instrumentation.

Eight of the Phase II round robin data sets were used in an ASTM E 691 calculation, the results of which are shown in Table 4-5. The precision parameters, r and R, in the table are much improved over those for the statistics for 11 data sets, shown in Table 4-4. As a way to compare these precision values with a known standard method of analysis for mercury, Table 4-6 lists the concentration ranges, repeatability, and reproducibility intervals calculated from the selected Phase II data and those from ASTM standard test method D 6414 (2). The slope (0.172) in the linear repeatability equation from the Phase II data is slightly higher than that in the equation for D 6414 (0.11). This information indicates the within-lab precision of the sorbent tube analyses is lower than that expected for D 6414 analyses of coal and combustion residues. However, the slope (0.233) in the linear reproducibility equation from the Phase II data is slightly lower than that in the equation for D 6414 (0.25). This information indicates the between-lab precision of the sorbent tube analyses is higher than that expected for D 6414 analyses of coal and combustion residues. In summary, it can be stated that the selected Phase II round robin data sets give precision statements very similar to those obtained in ASTM standard test method D 6414.

Table 4-5
Statistical Parameters for Selected Phase II Data Calculated by ASTM E 691

Labs	Average (ng)	Sr	SR	Suspect k	Suspect h	r	R
8	236	20	32	1	0	56	90
8	2329	124	307	1	0	348	859
8	8524	423	852	0	0	1185	2387
8	23630	1364	2121	1	0	3819	5938
8	37485	2311	3163	1	1	6471	8857

Table 4-6
Comparison of Estimated Repeatability and Reproducibility Intervals for Selected Phase II Data with ASTM D 6414

Method	Concentration Ranges	Repeatability, r	Reproducibility, R
Phase II	236-37,485 ng/tube = 118-18,740 ppb	Y = 0.172x - 113	Y = 0.233x + 260
D 6414 (for coal)	0.032-0.585 ppm = 32-585 ppb	Y = 0.11x + 0.012	Y = 0.25x + 0.003

Where x = average of 2 successive analyses

4.3.2 Evaluation of Phase II Data by Appendix K Criteria

Appendix K stipulates that laboratories must demonstrate that they can achieve a percent recovery of 85-115% at three spike levels, prior to beginning analyses of sorbent tube samples. Eight of the 11 laboratories met this criterion for three or more of the six spiking levels. Three laboratories using the Modified M6414 method did not meet this criterion. Appendix K does not stipulate the levels to be included in the spike recovery study; if the 40 ng spike had been selected as one of the three spike levels, only three of the 11 labs would have met the criterion.

As discussed earlier, there are known factors that contributed to the low recoveries reported by each of the labs submitting the Modified M6414 data sets. Some labs were able to meet the Appendix K criterion using Modified M6414, which indicates that this method is suitable for this purpose. However, it appears that laboratories using M6414 will have to pay more attention to optimizing extraction conditions and instrumentation than will laboratories using the other methods.

4.3.3 Evaluation of Laboratory Background Mercury

Each participating laboratory was asked to analyze the B sections of the sorbent tubes to check for breakthrough and help establish a background mercury level for their laboratory. Figure 4-7 shows the average amounts of mercury in the B sections for each spike level, as analyzed by the four different methods. Some laboratories did not submit B section data. It should be noted that only a few of the labs have true clean lab conditions for mercury.

Some methods appear to be more sensitive to background mercury levels than others. For example, the Direct Combustion Method uses all solids for calibration (NIST SRMs) and analysis, thus avoiding possible contamination introduced through liquid reagents, containers and dilution practices. Therefore, the background mercury is lower with this method.

Most of the analytical methods show higher mercury in the B sections from higher spike level samples. Much of this can be attributed to the calibration and instrument performance while working at the higher mercury levels. Analysis of low levels of mercury with an instrument specifically calibrated for high mercury levels introduces high error, and a resulting positive bias. An alternative explanation for the high blanks at high spike levels, breakthrough during spiking, can be eliminated by the results of the direct combustion analysis. In that method, all blank samples were run with a calibration at a low mercury level and a high sensitivity, and had equally low results for the B sections of all samples.

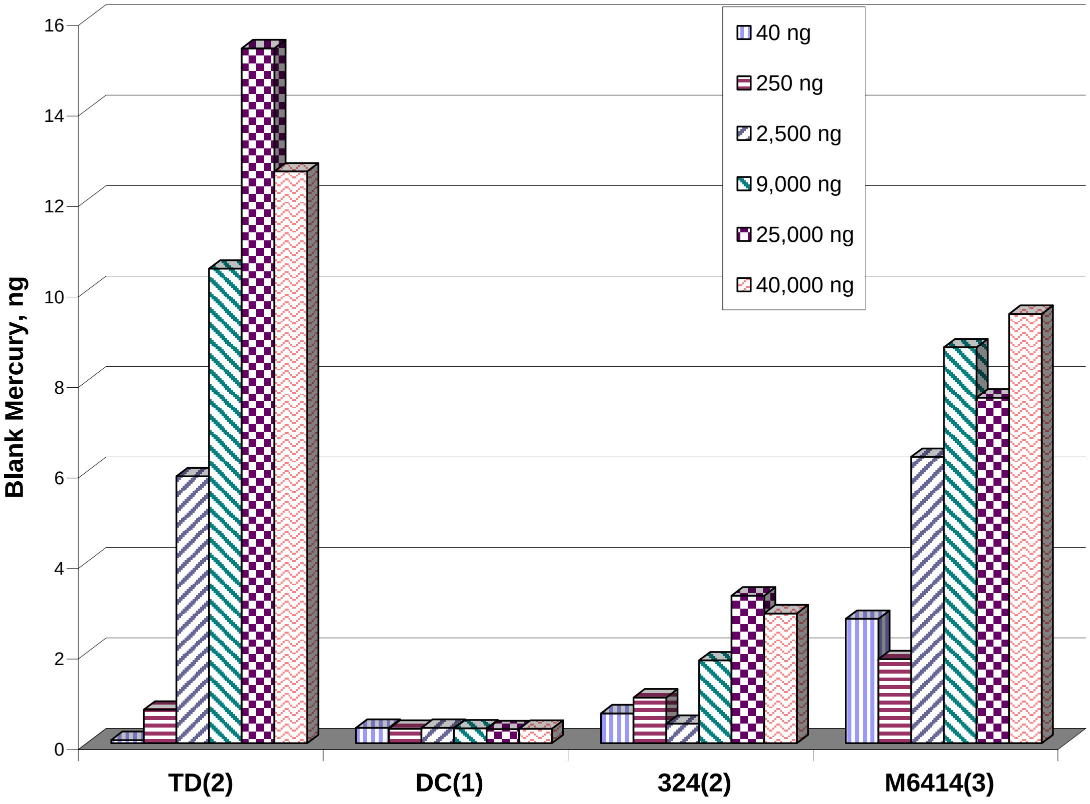

Figure 4-7
Average Blank Mercury Level, by Spike Level and Method (Number of Labs)

Due to the calibration issue, the results of B sections analyzed along with the lowest spike levels are the best indicator of the background mercury levels achieved by each lab. Figure 4-8 shows the Phase II blanks associated with the 40 ng and 250 ng spikes, for eight of the Phase II labs. Two labs did not report blanks, and one could not detect mercury at this low level. Most of the blanks were below 5 ng per section, and a large percentage were below 1 ng.

Appendix K does not specify a quality control criterion for blanks, but stipulates that the mercury measured in sorbent tube sections A and B must be summed together to report a total mercury loading in the sample. There is no provision for correcting results for a sorbent tube blank. Thus, if the background contribution to the mercury in each section is 5 ng, that will result in 10 ng of mercury added to the reported mercury value. Whether or not any given background level is significant depends on the stack emissions rate and sampling duration. A 10 ng background contribution would not be significant for a 10,000 ng tube loading, but would be for a two-hour sample on a low-emitting stack, which might collect less than 100 ng. For this reason, laboratories that plan to analyze short-duration samples may need to implement clean room conditions and evaluate mercury contributions from reagents and other sources.

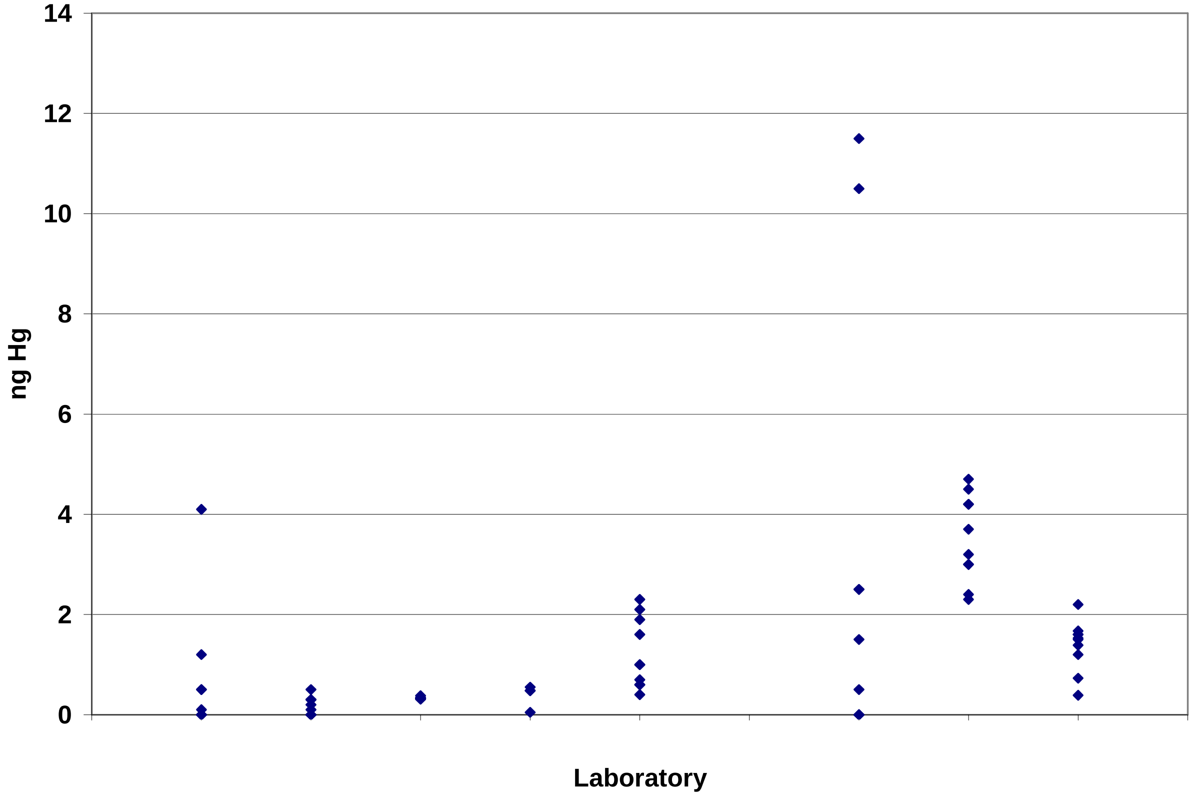

Figure 4-8
Mercury in Blanks from the Lowest Two Spike Levels

4.4 Discussion of Phase II Results

The interlaboratory study conducted during Phase II of this project demonstrated that acceptably accurate measurements of mercury captured on iodide-treated activated carbon sorbent material can be obtained by any one of four analytical methods:

- Draft EPA Method 324/AFS
- Modified ASTM Method D 6414 – Acid Extraction/AAS or AFS
- Ohio Lumex Thermal Desorption/AAS
- Direct Combustion Analysis/AAS - Modified ASTM Method D 6722

For each of these methods, at least one laboratory achieved better than 95% recovery of mercury from spiked sorbent tubes at spike levels between 250 ng and 40,000 ng of mercury. These results indicate that meeting Appendix K criteria for spike recovery will be possible with any of the methods.

At the 40 ng spike level, the variability in the mercury measurements was much higher than for the other spike levels. This indicates that the methods may be operating below their working range. This study was not designed to measure the detection limits or quantitation limits for sorbent tube mercury analysis methods, but the results do indicate a concern for the application of these techniques to very low-emitting stacks or for short-duration samples. This is a significant issue for sorbent tube analysis, as future reductions in mercury emissions will increase the proportion of low-emitting units.

There are some measures that can be taken to improve precision at low mercury levels. Due to the round robin study design, most labs calibrated their instruments over a wide range of concentrations, which means that measurements at the outer ranges of the calibration had larger measurement errors. In practice, laboratories will generally know in advance the approximate mercury loading on a sample tube, and can calibrate their instrument over an appropriate, narrower range of concentrations.

Another approach to increasing method performance is to increase the sampling duration and/or the sampling rate, to increase the tube loading. If the sorbent tube method is approved by EPA as a reference method, the need for 2-hour RATA samples to match Ontario Hydro sampling may be eliminated. This will allow for longer duration samples in most circumstances.

The progression of work from Phase I into Phase II and beyond indicates there are several factors to consider and conditions that must be met to ensure accurate laboratory measurements of mercury in iodide-treated activated carbon tubes:

- Each laboratory needs to establish that their chosen method and analytical instrumentation is capable of achieving acceptable accuracy at the target levels of mercury loading.
- In the methods that produce acid extracts (Draft EPA Method 324 and Modified ASTM method D 6414), molecular iodine is a formidable chemical interferent in both AAS and AFS instruments. AFS can accommodate greater sample dilution, which can partially overcome this interference. It is essential to optimize the extraction conditions and sample dilution to minimize this interference. The very high acid concentrations used in Method 324 are very efficient at extracting the mercury from the activated carbon material in the sorbent tube. The high acid concentrations used by one lab employing the Modified D 6414 Method (30 mL of 50:50 HNO_3:HCl) are just as efficient.
- Some flow injection AAS instruments are not capable of detecting mercury at a tube loading below 250 ng in acid extract solutions that contain molecular iodine. This 250 ng level is five times greater than the 2-hour sample (48 ng) from a stack with 1 $\mu g/m^3$ mercury emissions at a 400 cc/min flow rate.
- For the thermal desorption (Ohio Lumex) procedure, the system needs to be calibrated using the exact matrix material and the same quantity of matrix used in the sample. Materials that change the burning profile of the carbon matrix will change the rate of thermal desorption of mercury, resulting in changes in the rate of mercury measurement and possible errors in the analysis.

- For the direct combustion method, low recoveries at the lowest (40 ng) spike level may indicate that some mercury was lost during the homogenization process. Further research is required to identify the source of the loss and identify remedial measures. The lower recovery at 40 ng is not likely to be related to instrument sensitivity. The limit of detection for the LECO AMA 254 under similar conditions is 0.2-0.5 ng (5). A 100 mg portion of a 1.7 gram sorbent bed spiked with ~40 ng of mercury contains ~ 2 ng of mercury, which is well above the instrument's limit of detection. If lower mercury loadings are expected, the sample size can be increased to 200 mg, or multiple sample burns can be conducted with one amalgamator cycle. Either of these procedures would increase the sensitivity of the instrument.

5

RECOMMENDATIONS FOR FUTURE STUDIES

Additional work that would benefit the project almost immediately would be to establish a method for homogenizing and subsampling of the solid sorbent material in the tubes. During the course of the project, a method for milling the sorbent carbon in a SPEX 8000D ball mill was developed by the LECO Corporation. The homogenized samples produced by this method were used in the direct combustion tests with the LECO AMA 254 Mercury Analyzer. The % RSDs obtained with this method were generally were generally less than 3%. A follow-up study to evaluate the homogenation and subsampling procedure for use in other test methods is planned. Homogenation would allow smaller samples to be used for :

- acid extraction methods, thus providing backups for sample loss
- thermal desorption, to avoid data loss and eliminate the requirement to split large tube beds into two sections for analysis

Homogenation would also allow for acid extraction of a smaller mass of carbon. Research at Consumers Energy (5) during the course of this project showed that the amount of mercury extracted from the iodide-treated carbon is dependent on the mass of carbon material used in the extraction process. Figure 5-1 shows that in the Consumers Energy study, the percentage of mercury extracted decreased from 97% to 76% as the amount of carbon was increased from 0.5 to 2.5 g. All other conditions, such as the amount of acid used, heating time, and solution volume (50 mL) were kept constant. It was verified that the missing mercury was retained on the carbon, and could be detected by repeat extraction of the carbon residue.

This study provides very strong evidence for the need to reduce the amount of sorbent material extracted (currently about 1.7 g) relative to the solution volume in the two extraction methods. It also indicates that a laboratory cannot assume that they will achieve equal extraction efficiency with different sizes of carbon tube. Since one commercial supplier of Appendix K tubes has recently reduced the “A” section size from 1.7 g to 1 g, laboratories should confirm their performance on the new mass of sorbent.

Further research is needed into ways to minimize the iodine interference during mercury analysis. Dilution of the extract solutions is the only method currently known to minimize the problem. Developing of a procedure to accurately access this interference is needed. The method of sample addition, recommended during Phase II, may be the answer needed. This procedure was not widely implemented during the round robin study, so the potential improvement using this approach remains to be determined.

Further work on the analysis of samples obtained from low level sampling is needed, especially by those labs who plan to use one (or more) of the four methods as a reference method (pending EPA approval). Some of the labs that participated in this study have already begun this work and have lowered their detection levels by systematically making the modifications needed to reach the levels needed for reference method samples.

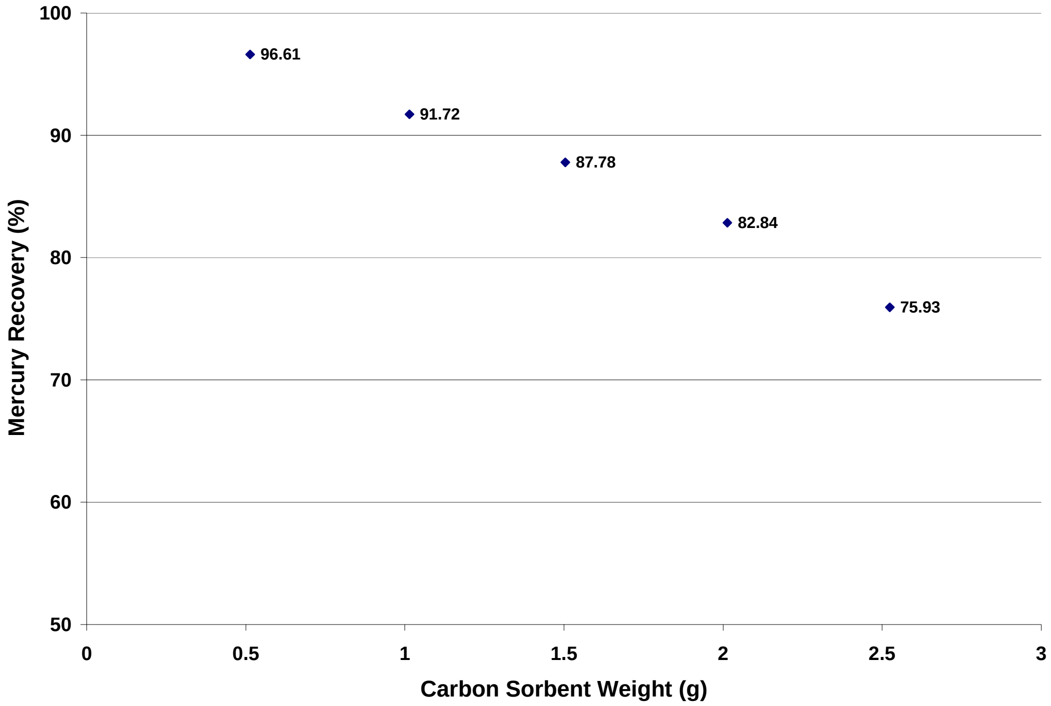

Figure 5-1
Percent of Mercury Recovered as a Function of Sorbent Mass Extracted

There is a possibility that some types of analytical instruments are not able to overcome the problems of iodine interference and sensitivity of measurements at very low mercury levels. Some of these problems may be worsened by the tendency of lab personnel to use the analytical instrumentation over wide calibration ranges. All analytical instruments used in this project have a most sensitive analytical range. All of them also have expanded ranges with built in algorithms that simulate linear behavior over the entire range. The largest measurement errors occur at the extremes of the calibration curve, and some of these simulated linear plots use exponential correction terms. Thus, the errors near the extremes of these plots increase exponentially. Instrument operators need to exercise more caution in using the expanded range instruments for low- and high-level measurements.

A preferred approach is for laboratories to dilute the extracts appropriately, so that the analyses can be conducted in their instrument's most sensitive analytical range. This could require an extra screening analysis to select the correct dilution, but in routine practice, power plant facilities should know in advance the expected loading on any given mercury tube, to the extent needed to select a dilution.

A

MERCURY SPIKING AND ANALYTICAL METHODS

A.1 Method For Spiking Elemental Mercury On Iodated Carbon Tubes

This technique is based on the premise that stannous chloride ($SnCl_2$) in solution converts 100% of Hg^{+2} in solution to gaseous Hg^0. The gaseous Hg^0 is then transported to the iodated carbon tube where it is chemically bonded to the surface of the carbon.

EQUIPMENT

- Two glass impingers in series are connected by PFA tubing, followed by a pump with a flow meter able to accurately control the gas flow through the impingers. The first impinger is a modified Smog bubbler (commercially available from Ace Glass, Part #7529). The bubbler must be modified by removing the inlet arm and connecting a straight ¼" piece of glass, and the outlet arm must be cut and a ¼" piece of glass added. Any knock-out impinger can be used for the second impinger. The bubbler system is shown in Figure A-1.
- Adjustable pipetter capable of accurately delivering NIST Hg salt standard solution.

CHEMICALS

- NIST traceable mercuric nitrate ($Hg(NO_3)_2$ standard solution. A mercuric chloride ($HgCl_2$) solution would also have been an acceptable for of mercury.
- Trace metal grade hydrochloric acid.
- ACS grade stannous chloride.
- Deionized water.

PROCEDURE

1. Attach the iodated carbon tube to the exit of the second impinger, making sure the section to be spiked is towards the impinger. (See Figure A-2)
2. Using a graduated cylinder, transfer 100 ml of room temperature deionized water into the first impinger. In order to accomplish this, the stem with frit must be removed, as shown in Figure A-3.
3. Pipette a NIST-traceable, Hg salt standard of appropriate concentration into the first impinger, making sure the standard is pipetted directly into the water. Immediately re-insert the stem with frit into the first impinger and connect the vacuum line to the second impinger. The vacuum should be pre-set to pull room air through the impinger system at a rate of 1000 cc/min.

4. Pipette 1 ml of 12.5% stannous chloride (w/v) with 6% hydrochloric acid down the center stem of the first impinger (See Figure A-4), then flush the stem with a small amount of deionized water. Bubble room air through the tube for at least 30 minutes for loadings of <10,000 ng of mercury and for 1 hour for loadings •10,000 ng of mercury. Shorter times may not evolve all of the mercury from the stannous chloride solution onto the iodated carbon tube. Turn off vacuum and remove iodated carbon tube.

   ***Note**: The NIST traceable Hg salt standard solution should be diluted to an appropriate concentration so that 2 to 4 ml of the standard is spiked into the stannous chloride solution. If the volume is less than 2 ml or more than 4 m, there may not be complete conversion to elemental mercury.*

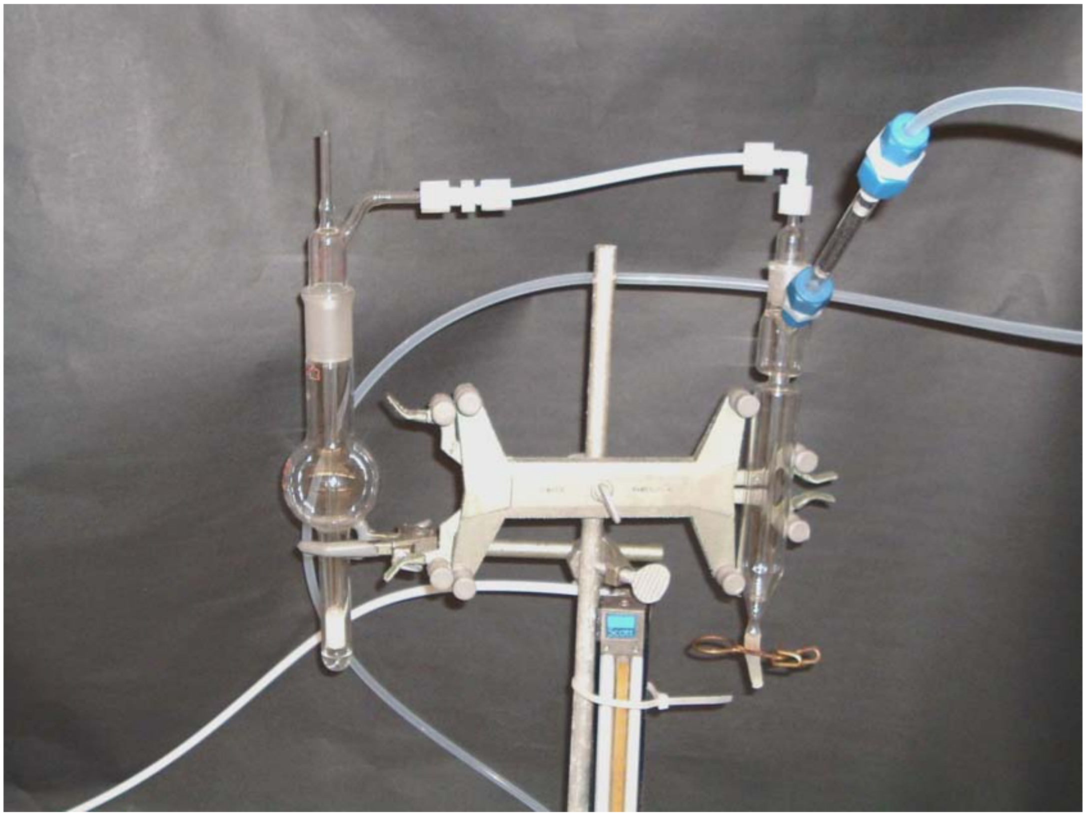

Figure A-1
Sorbent tube spiking system

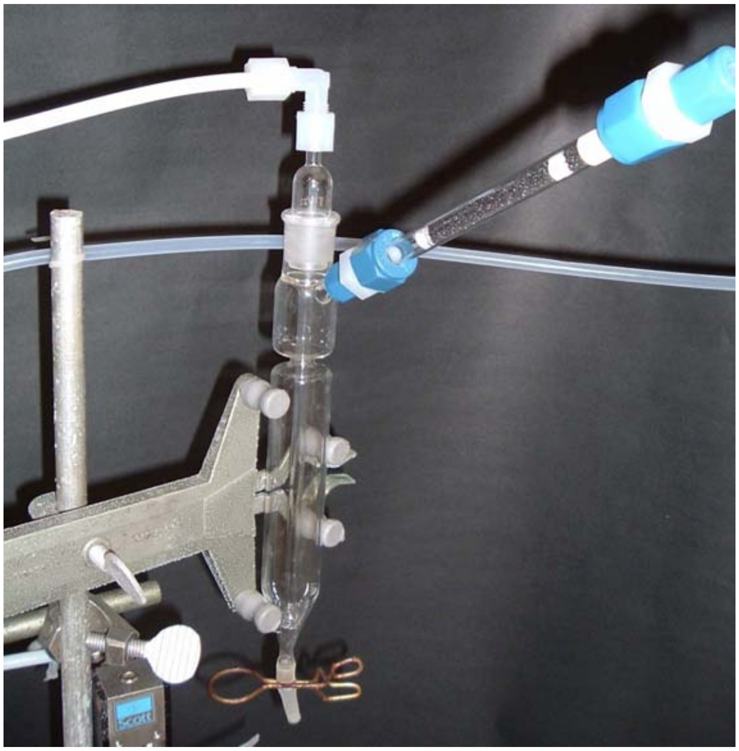

Figure A-2
Sorbent tube connected to exit of second impinger

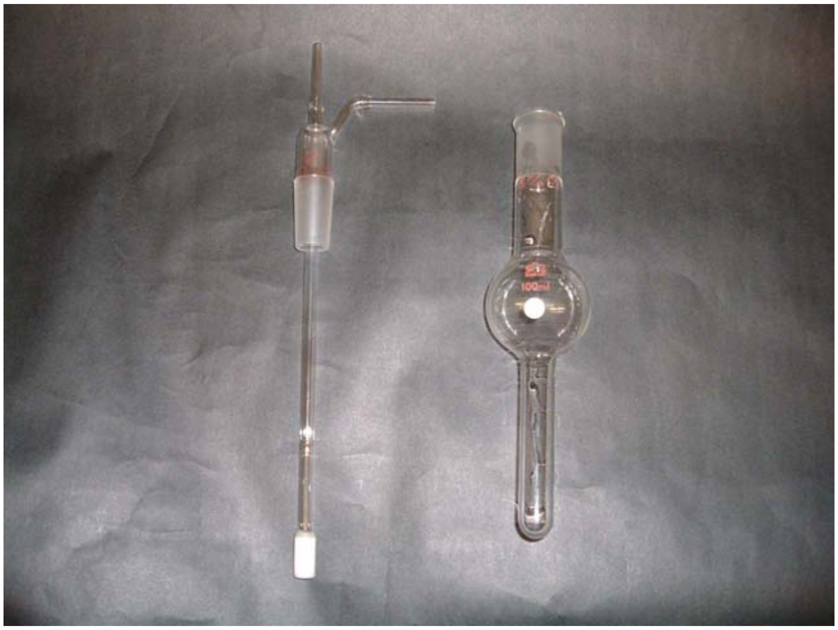

Figure A-3
First impinger with stem removed

Figure A-4
First impinger stannous chloride injection point

A.2 Draft EPA Method 324

Draft Method 324

Determination of Vapor Phase Flue Gas Mercury Emissions from Stationary Sources Using Dry Sorbent Trap Sampling

SUBSECTION: ANALYSIS METHOD BY CVAFS

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1.0 Introduction.

This method describes the analysis of samples collected for the determination of mercury (Hg) emissions in combustion flue gas streams using chemically impregnated charcoal sorbent traps. Only the cold vapor atomic fluorescence spectroscopy (CVAFS) analytical method is detailed in this document. Appendix A includes a discussion of other analysis methods. Currently, the only validated detection system for Method 324 is CVAFS. The CVAFS procedure is similar in principal to EPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry.

1.1 Scope and Application.

1.1.1 Analytes. The analyte measured by this method is total vapor-phase Hg, which represents the sum of elemental (CAS Number 7439–97–6) and oxidized forms of Hg in mass concentration per air volume for indoor and ambient air and flue gas samples.

1.1.2 Applicability. This analysis method is applicable to the determination of vapor-phase Hg concentrations ranging from 0.03 to 100 micrograms per cubic meter ($\mu g/m^3$) collected on chemically impregnated charcoal sorbent traps. The matrix may be indoor air, ambient air or combustion flue gas. Suggested sampling flow rates are 0.2 – 0.6 L/min and an appropriate sampling time to assure that a minimum of 5.0 ng Hg has been collected on the trap. The sample should not contain appreciable amounts of flyash. The accuracy of the entire method is directly proportional to the accuracy of the measured sample volume.

2.0 Summary of Method.

Accurately known volumes of air or flue gas are pulled under vacuum through chemically impregnated charcoal sorbent traps with a nominal flow rate of 0.2 to 0.6 liters per minute. Each trap is then acid leached and the resulting leachate is analyzed by CVAFS detection. The proper technique for the collection of the samples is critical to the success of the entire method. This document does not describe sample collection procedures.

3.0 Definitions. [Reserved]

4.0 Clean Handling and Contamination.

Preventing samples from becoming contaminated during the sampling and analysis process constitutes one of the greatest difficulties encountered in trace metals determinations. Therefore, it is imperative that extreme care be taken to avoid contamination when preparing, collecting, transporting and analyzing samples for trace metals.

4.1 *Contamination Summary.* Samples may be contaminated by numerous routes. Potential sources of trace metals contamination include: metallic or metal-containing labware (e.g., talc gloves that contain high levels of zinc), containers, sampling equipment, reagents, improperly cleaned or stored equipment, labware, reagents and atmospheric inputs such as dirt and dust. Even human contact can be a source of trace metals contamination. Therefore, it is imperative that the procedures described in this method are carried out by well-trained, experienced personnel.

4.2 *Contamination Control.*

4.2.1 *Philosophy* – The philosophy behind contamination control is to ensure that any object or substance that contacts the sample is metal free and free from any material that may contain mercury.

4.2.2 *Avoiding Contamination* – The best way to control contamination is to completely avoid exposure of the sample to contamination in the first place. Avoiding exposure means performing operations in an area know to be free from contamination. Two of the most important factors in avoiding/reducing sample contamination are (1) an awareness of potential sources of contamination and (2) strict attention to work being done. Care must be taken to avoid touching other potentially contaminated surfaces when handling the sorbent trap.

4.2.3 *Use a clean environment* - The ideal environment for processing samples is a class-100 clean room. If a clean room is not available, all sample preparation should be performed in a class-100 clean bench with a nonmetal glove box fed by mercury-and particle-free air or nitrogen. Digestion should be performed in a fume hood in a laboratory know to have air mercury concentrations below 25 g/m^3.

4.2.4 *Minimize exposure* – Apparatus that will contact samples, blanks or standard solutions should be opened or exposed only in a clean room, clean bench, or glove box so that exposure to an uncontrolled atmosphere is minimized.

4.2.5 *Clean work surfaces* – Before a given batch of samples is processed, all work surfaces in the hood, clean bench, or glove box in which the samples will be processed should be cleaned.

4.2.6 *Wear gloves* – Sampling personnel must wear clean, non-talc gloves during all operations involving handling of samples, and blanks.

4.2.7 *Use metal-free apparatus* - All apparatus used for determination of mercury must be nonmetallic, free of material that may contain metals, or both.

4.2.8 *Contamination by airborne particulate matter* - Samples may be contaminated by airborne dust, dirt, particles, or vapors from unfiltered air supplies; nearby corroded or rusted pipes, wires, or other fixtures; or metal-containing paint. Whenever possible, sample collection, processing and analysis should occur as far as possible from sources of airborne contamination. Laboratory air should be monitored routinely (monthly) and be below 25 ng/m^3.

4.2.9 *Use appropriate reagents* - During analysis it is possible to introduce contamination into samples from method reagents used during processing and analysis. Reagent blanks must be analyzed for contamination prior to use. If reagent blanks are contaminated, a new batch of reagents must be prepared.

4.2.10 *Analytical contamination* - Contamination can also occur during analysis as a result of carryover when a sample containing a low concentration of mercury is processed immediately after a sample containing a relatively high concentration of mercury. Due to the potential for widely varied concentrations, it is important to understand when sample carry-over is likely to occur and provide assurance that the analytical system remains in control.

5.0 Safety.

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 OSHA Regulations. Laboratory safety policies that meet OSHA regulations to minimize risk of chemical exposure must be followed.

5.3 Toxicity and Carcinogenicity. The toxicity or carcinogenicity of reagents used in this method has not been fully established. The procedures required in this method may involve hazardous materials, operations, and equipment. This method may not address all of the safety problems associated with these procedures. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicable regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies.

6.1 Sorbent Trap. The sorbent trap should be obtained from a reliable source that has clean handling procedures in place for ultra low-level Hg analysis. This will help assure the low Hg environment required to manufacture the sorbent traps with a low and consistent Hg content necessary for accurate results. Sorbent trap sampling requirements or needed characteristics are shown in Table 324–1 and Figure 324-1. Selection of the sorbent trap shall be based on: (1) Achievement of the performance criteria of this method, and (2) data is available to demonstrate the method can pass the criteria in EPA Method 301 when used in this method and when the results are compared with those from EPA Method 29, EPA Method 101A, or ASTM Method 6784–02 for the measurement of vapor-phase Hg in a similar flue gas matrix. Appropriate traps are referred to as ‘‘sorbent trap’’ throughout this method. The method requires the analysis of Hg in both main and backup portions of the sorbent within each trap. The sampled sorbent trap is the entire Hg sample.

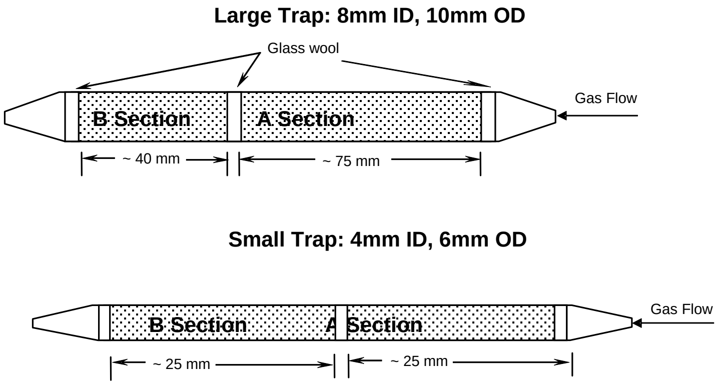

Figure 324-1
Dimensions and configuration of the existing FSTM sorbent trap that was used to validate Method-324

Table 324-1
Specifications and performance criteria for the FSTM sorbent traps which were used to validate M-324

Item to Be Determined	Small Sorbent Trap	Large Sorbent Trap
Frontier FSTM – proprietary chemically treated charcoal	300 mg in 0.55 cm^3 0.55 cm^3 ± 20% in two beds	2800 mg in 5.5 cm^3 ± 20% in two beds
Trap size	Inner Diameter ~4 mm	Inner Diameter ~8 mm
Trap Quality Indicator (including all reagent contributions)	<2.0 ng/trap ± 1.0 ng/trap (n•3)	<2.0 ng/trap ± 1.0 ng/trap (n•3)

6.2 *Cold Vapor Atomic Fluorescence Spectrometer (CVAFS):* The CVAFS system may either be purchased from a supplier, or built in the laboratory from commercially available components.

6.2.1 *Commercially available CVAFS*. Tekran (Toronto, ON) Series 2500 CVAFS, Brooks-Rand (Seattle, WA) Model III CVAFS, Leeman Labs Hydra AF Gold *plus* CVAFS, or equivalent. Automated systems, for example the Tekran 2600 series, are also acceptable. However, the automated systems may require additional chemical treatment to prevent matrix interferences that are not described in this manual method.

6.2.2 *Custom-built CVAFS*. Figure 324-2 shows the CVAFS schematic diagram. The system consists of the following:

6.2.2.1 Low-pressure 4-W mercury vapor lamp

6.2.2.2 Far UV quartz flow-through fluorescence cell – 12 mm x 12 mm X 45 mm, with a 10 mm path length (NSG Cells, or equivalent).

6.2.2.3 UV-visible photomultiplier (PMT)—sensitive to < 230 nm. This PMT is isolated from outside light with a 253.7- m interference filter (Oriel Corp., Stamford, CT, or equivalent).

6.2.2.4 Photometer and PMT power supply (Oriel Corp., or equivalent), to convert PMT output (nanoamp) to millivolts.

6.2.2.5 Black anodized aluminum optical block—holds fluorescence cell, PMT, and light source at perpendicular angles, and provides collimation of incident and fluorescent beams (Frontier Geosciences Inc., Seattle, WA, or equivalent).

6.2.2.6 Flowmeter—with needle valve capable of reproducibly keeping the carrier gas flow rate at 30 mL/min.

6.3 Hg purging system. Figure 324-2 shows the schematic diagram for the purging system. The system consists of the following:

6.3.1 Flow meter/needle valve –capable of controlling and measuring gas flow rate to the purge vessel at 350 ± 50 mL/min.

6.3.2 Fluoropolymer fittings—connections between components and columns are made using 6.4-mm OD fluoropolymer tubing and fluoropolymer friction-fit or threaded tubing connectors. Connections between components requiring mobility are made with 3.2-mm OD fluoropolymer tubing because of its greater flexibility.

6.3.3 Acid fume pre-trap — 10-cm long x 0.9-cm ID fluoropolymer tube containing 2-3 g of reagent grade, non-indicating, 8-14 mesh soda lime, packed between wads of silanized glass wool. This trap is cleaned of Hg by placing on the output of a clean cold vapor generator (bubbler) and purging for 1 hour with N_2 at 350 mL/min. This acid fume trap is critical to protect the gold-quartz. The proper functioning of the acid fume pre-trap is critical to avoid Hg losses or contamination of samples.

6.3.4 Cold vapor generator (bubbler)—150-mL borosilicate glass (15 cm high x 5.0 cm diameter) with standard taper 24/40 neck, fitted with a sparging stopper having a coarse glass frit that extends to within 0.2 cm of the bubbler bottom (Frontier Geosciences, Inc., or equivalent).

6.4 The dual-trap Hg^0 preconcentrating system

6.4.1 Figures 324-2 shows the schematic setup of the dual-trap amalgamation system.

6.4.2 Gold-coated quartz traps—10 cm long X 6.5 mm OD x 4-mmID quartz tubing. The tube is filled with 3.4 cm of gold-coated 45/60mesh quartz chips (Frontier Geosciences Inc., Seattle, WA, or equivalent). The ends are plugged with quartz wool.

6.4.2.1 Traps are fitted with 6.5-mm ID fluoropolymer friction-fit sleeves for making connection to the system. When traps are not is use, fluoropolymer end plugs are inserted in trap ends to eliminate contamination.

6.4.2.2 At least six traps are needed for efficient operation, one as the "analytical" trap, and the others to sequentially collect samples

6.4.3 Heating of gold-coated sand traps—To desorb Hg collected on a trap, heat for 2.0 min to 450-500°C (a barely visible red glow when the room is darkened) with a coil consisting of 75 cm of 24-gauge Nichrome wire at a potential of 10-14 VAC. Potential is applied and finely adjusted with an autotransformer.

6.4.4 Timers—The heating interval is controlled by a timer-activated 120-V outlet (Gralab, or equivalent), into which the heating coil autotransformer is plugged. Two timers are required, one each for the "sample" trap and the "analytical" trap.

6.4.5 Air blowers-After heating, traps are cooled by blowing air from a small squirrel-cage blower positioned immediately above the trap. Two blowers are required, one each for the "sample" trap and the "analytical" trap.

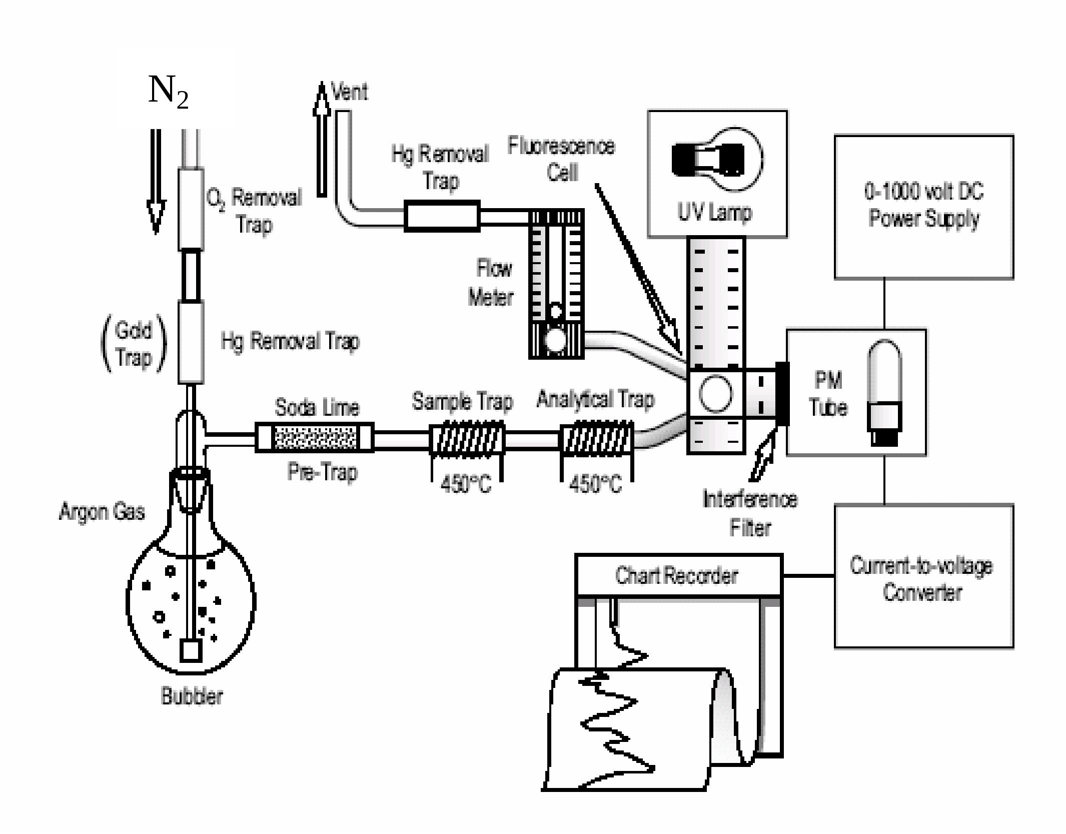

Figure 324-2
Schematic of the manual purging, dual-trap preconcentration and CVAFS detector for the determination of total mercury. An schematic of the automated version of this method can be found in EPA Method 1631, Rev E.

6.5 *Recorders.* Any multi-range millivolt chart recorders or integrator with a range compatible with the CVAFS is acceptable. By using a two-pen recorder the dynamic range of the system can be set at a level of 10^3. Computer-based data acquisition systems are acceptable.

6.6 *Pipettors.* All-plastic pneumatic fixed-volume and variable pipettors in the range of 10 µL to 5.0 mL.

7.0 Analysis by CVAFS, Reagents and Standards.

<u>Note:</u> The quantities of reagents and the preparation procedures in this section are for illustrative purposes. Equivalent performance may be achievable using quantities of reagents and procedures other than those suggested here. The laboratory is responsible for demonstrating equivalent performance.

7.1 *Reagent Water.* 18-M minimum, ultrapure deionized water starting from a prepurified (distilled, reverse osmosis, etc.) source. Water should be monitored for Hg, especially after ion exchange beds are changed.

7.2 Laboratory Air. It is very important that the laboratory air be low in both particulate and gaseous mercury. Ideally, mercury work should be conducted in a new laboratory with mercury-free paint on the walls. A source of air that is very low in Hg should be brought in directly into the Class-100 clean bench air intake. If this is not possible, air coming into the clean bench can be cleaned for mercury by placing a gold-coated cloth prefilter over the intake. For specific instructions on how to fabricate the gold coated cloth, please refer to Method 1631e section 7.2

7.3 Hydrochloric Acid. Trace-metal purified reagent-grade HCl containing less than 5 g/mL (picogram/ml) Hg. The HCl should be analyzed for Hg before use.

7.4 Stannous Chloride. Bring 200 g of $SnCl_2.2H_2$0 and 100 mL concentrated HCl to 1.0 L with reagent water. Purge overnight with mercury-free N_2 at 500 mL/min to remove all traces of Hg. Store tightly capped.

7.5 Bromine Monochloride (BrCl, 0.2N). In a fume hood, dissolve 27 g of reagent grade KBr in 2.5 L of low-Hg concentrated HCl. Place a clean Teflon-coated magnetic stir bar in the bottle and stir for approximately 1 h in the fume hood. Slowly add 38 g reagent grade $KBrO_3$ to the acid while stirring. When all of the $KBrO_3$ has been added, the solution color should change from yellow to red to orange. Loosely cap the bottle, stirring another hour before tightening the lid. ***WARNING:*** *This process generates copious quantities of free halogens (Cl_2, Br_2, BrCl), which are released from the bottle. Add the $KBrO_3$ slowly in a fume hood!*

7.6 5% Solution of Bromine Monochloride (BrCl). Accurately mix 125 ml of 0.2N BrCl into 2.375 L of low-Hg Reagent Water (section 7.1).

7.7Hg Standards.

7.7.1 Stock mercury standard – NIST-certified 10,000-ppm aqueous Hg solution (NIST-3133). This solution is stable at least until the NIST expiration date.

7.7.2 Secondary Hg standard – Add approximately 0.5 L of reagent water and 20 mL of BrCl solution (Section 7.5) to a 1.00-L Class A volumetric flask. Add 0.100 mL of the stock mercury standard (Section 7.7.1) to the flask and dilute to 1.00 L with reagent water. This solution contains 1.00 µg/mL (1.00 ppm) Hg. Transfer the solution to a fluoropolymer bottle and cap tightly. This solution is considered stable until the NIST expiration date.

7.7.3 Working Hg Standard A – Dilute 1.00 mL of the secondary Hg standard (section 7.7.2) to 100 mL in a Class A volumetric flask with reagent water containing 2% by volume BrCl solution (Section 7.5). This solution contains 10.0 ng/mL and should be replaced monthly, or longer if extended stability is demonstrated.

7.7.4 Working Hg Standard B – Dilute 0.10 mL of the secondary Hg standard (section 7.7.2) to 1000 mL in a Class A volumetric flask with reagent water containing 2% by volume BrCl solution (Section 7.5). This solution contains 0.10 ng/mL and should be replaced monthly, or longer if extended stability is demonstrated.

7.7.5 Initial Calibration Verification (ICV) Standard - A second standard must be prepared to act as an independent check of the calibration standard. The ICV standard must be purchased from a supplier other than NIST to assure that the solutions are truly independent of each other. The standard should be diluted as described in section 7.7.2 and 7.7.3 to reduce the concentration to an acceptable working range. It is advised to have a final concentration other than 10 g/mL, so that the ICV and working standard have unique concentrations.

7.8 Nitric Acid. Trace-metal purified reagent-grade HNO_3 containing less than 5 pg/mL Hg. The HNO_3 should be analyzed for Hg before use.

7.9 Sulfuric Acid. Trace-metal purified reagent-grade H_2SO_4 containing less than 5 pg/mL Hg. The H_2SO_4 should be analyzed for Hg before use.

7.10 Nitrogen. Grade 4.5 (standard laboratory grade) nitrogen that has been further purified by the removal of Hg using a gold-coated sand trap.

7.11 Argon. Grade 5.0 (ultra high-purity, GC grade) argon that has been further purified by the removal of Hg using a gold coated sand trap.

8.0 Field Sample Collection and Transport.

The purpose of this document is to describe the analysis method only. Refer to Appendix K for specific procedures for sample collection and transport. The proper sample collection and transport of samples is required to obtain accurate and precise results for the overall method. Sample collection may include trip blanks, field blanks and field spikes, that must be analyzed as a normal sample as described in this procedure.

9.0 Quality Control.

Table 324-2 summarizes the laboratory QC components required by Appendix K. QC requirements affecting sampling alone are not included. Table 324-3 recommends additional QC measures that will improve laboratory performance. The criteria shown in this table are those used by Frontier Geosciences and should be evaluated by each individual laboratory with respect to their own procedures and data quality objectives.

9.1 The _reagent blank_ represents the Hg contribution from the digestion vessel, acids, and reagents used in the digestion and analysis of samples. Three reagent blanks are prepared with each digestion batch and the average is subtracted from all samples - see section 12.0.

9.2 The _sorbent trap blank_ is an optional measurement and represents the Hg contribution from the sorbent material only. This value does not include the Hg contributions from digestion vessels, acids, or reagents. This value becomes important in instances where the expected trap loading is <100 ng/trap, the field blank is high and variable or the trap quality is uncertain and variable (See Table 324-1). The average sorbent trap blank may be subtracted from the sample traps of the same lot. At least 3 sorbent traps blanks should be determined in order to assess statistical variability, since the values may be close to the method detection limit - see section 12.0

9.3 The _sorbent trap field blank_ is intended as a measurement of the Hg content present on the trap as a result of trap handling, deployment and collection of the trap, leak check, as well as sampling environment. One sorbent trap field blank is collected per 10 sample traps. This measurement is intended as a quality check of the sampling process only and is not used for blank correction purposes.

9.4 The _B Section (section 2 in Appendix K) analysis_ gives an indication of trap performance during the sampling period by assuring the sampling parameters (flow rate, collection time, moisture control, etc.) were compatible with the sorbent trapping capacity. If sampling parameters were followed, nominally greater than 99% of the Hg will be retained on the A Section. The Hg contained on the B Section is added to the A Section contribution to obtain the total Hg captured per trap – see section 12.0

Table 324-2.
Appendix K quality assurance and quality control criteria for sorbent tube analysis

QA/QC specification	Acceptance Criteria	Frequency	Corrective Action
Sorbent trap section 2 breakthrough	•5% of Section 1 mass	Every sample	Sample invalidated
Spike recovery study	Average recovery between 85% and 115% for each of the 3 spike concentration levels	Prior to analyzing field samples and prior to use of new sorbent media	Field samples shall not be analyzed until the percent recovery criteria have been met
Multipoint analyzer calibration	Each analyzer reading within ±10% of true value and r^2 •0.99	On the day of analysis, before analyzing any samples.	Recalibrate until successful
Analysis of independent calibration standards	Within ±10% of true value	Following daily calibration, prior to analyzing field samples	Recalibrate and repeat independent standard analysis until successful
Spike recovery from Section 3 of sorbent trap	75-125% of true value	Every sample	Sample invalidated

Note: criteria for laboratory analysis – additional criteria apply to sampling procedures

Table 324-2.
Additional quality assurance and quality control criteria for sorbent tube analysis

QA/QC specification	Acceptance Criteria	Frequency	Corrective Action
Reagent Blank	<5 ng/digest and a standard deviation of 1.0 ng/digest. (n=3)	3 per analysis set of 20 sorbent traps	Reanalyze, investigate source of high levels
Sorbent Trap Blank	<5 ng/digest and a standard deviation of 1.0 ng/digest. (n=3)	Not required, but recommended for low sample trap loadings (<100 ng/digest) or if field blanks or the trap quality indicator are above their acceptance criteria	A high sorbent trap blank may result in a positive bias. Investigate trap blank source and correct
Sorbent Trap Field Blank	<5 ng/trap or < 5% of average Hg collected on the traps.	1 per 10 field samples collected	Notify field personnel of sample handling issue, retrain. Also possible that the sorbent trap blank is contributing, investigate
Laboratory Analytical and Analytical Spike Duplicate (AS/ASD)	75-125% recovery with RPD ≤ 25 1 per analytical batch • 20 samples	1 per batch of 20 samples	Reanalyze, halt analysis and investigate possible instrumental causes of error, flag data if not resolvable
Laboratory Analytical Duplicate (AD)	• 20 RPD/RSD	1 per batch of 20 samples	Reanalyze, halt analysis and investigate possible instrumental causes of error, flag data if not resolvable

9.5 General note about instrument blanks. Due to the potential for high sample concentrations, the concentration at which the analytical system will carry Hg into the succeeding sample must be determined. This is accomplished by analyzing calibration solutions containing successively larger concentrations of Hg. This test must be run prior to first use of the analytical system and whenever a change is made that could potentially affect carryover. Whenever a sample contains ½ or greater of this determined Hg concentration, a bubbler blank (bubbler system) or system blank (flow injection system) must be analyzed to demonstrate no carryover at the blank criteria level. For a bubbler system, the blank must be run using the same bubbler and sample trap used to run the high concentration sample. Samples analyzed following a sample that has been determined to result in carryover must be reanalyzed. Samples that are known or suspected to contain the lowest concentration of mercury should be analyzed first followed by samples containing the higher levels.

10 Calibration and Standards.

Calibration procedures provided here are for bubbler systems with CVAFS detection (Section 11.4.1). Other systems such as flow injection may be employed if they are able to meet the control requirements listed in this method. Only specific instructions for the bubbler system are presented in this document. All systems shall be calibrated using standards traceable to NIST Standard Reference Materials. A new calibration is required daily or after 12 hours has elapsed since the last valid calibration.

10.1 Bubbler System Calibration

10.1.1 Establish the operating conditions necessary to purge Hg from the bubbler and to desorb Hg from the traps in a sharp peak. Further details for operation of the purge-and-trap, desorption, and analysis are given in Sections 11.4.1.

10.1.2 The calibration must contain a minimum of five non-zero points and the results of analysis of three bubbler blanks. The lowest calibration point must be at the Minimum Level (ML). ***NOTE****: The purge efficiency of the bubbler system approaches 100% and is independent of volume at the volumes used in this method. Calibration of this system is typically performed using units of mass. For purposes of working in concentration, the volume is assumed to be 100 mL.*

11 Analytical Procedures.

11.1 Preparation Step. The sorbent traps are received and processed in a low-Hg environment (class-100 laminar-flow hood and gaseous Hg air concentrations below 25 g/m^3) following clean-handling procedures. Any dirt or particulate present on the exterior of the trap must be removed to avoid contamination of the sample. The sorbent traps are then opened and the sorbent bed(s) and any packing material are transferred to an appropriate sized trace-clean vessel. It is recommended that the height of the trace-clean vessel be at least 3 times the diameter to facilitate a refluxing action.

11.2 Leaching Step. The sorbent trap is then subjected to a hot-acid leach using a 70:30 ratio mixture of concentrated HNO_3/ H_2SO_4. The acid volume must be 40 percent of the expected end volume of the digest after dilution. The HNO_3/H_2SO_4 acid to carbon ratio should be approximately 35:1. The leachate is then heated at the bottom of the vessel to a temperature of 50 to 60 °C for 1.5 to 2.0 hours in the finger-tight capped vessels. This process may generate significant quantities of noxious and corrosive gasses and must only be performed in a well-ventilated fume hood. Care must be taken to prevent excessive heated leaching of the samples as this will begin to break down the charcoal material.

11.3 *Dilution Step.* After the leached samples have been removed from the hot plate and allowed to cool to room temperature, they are brought to volume with a 5% solution of BrCl (Section 7.6). As the leaching digest contains a substantial amount of dissolved gasses, add the BrCl slowly, especially if the samples are still warm. As before, this procedure must be performed in a properly functioning fume hood. The sample is now ready for analysis.

11.4 *Hg Reduction and Purging.* Other systems such as flow injection may be employed if they are able to meet the control requirements listed in this method. Only specific instructions for the bubbler system are presented in this document.

11.4.1 *Bubbler System.* Pipette an aliquot of the digested sample into the bubbler containing pre-blanked reagent water and a soda lime trap connected to the exhaust port. Add stannous chloride ($SnCl_2$) to reduce the aliquot and then seal the bubbler. Connect gold sample traps to the end of the soda lime trap as shown in Figure 324-3. Finally, connect the N_2 lines and purge for 20 minutes. The sample trap can then be added into the analysis cycle.

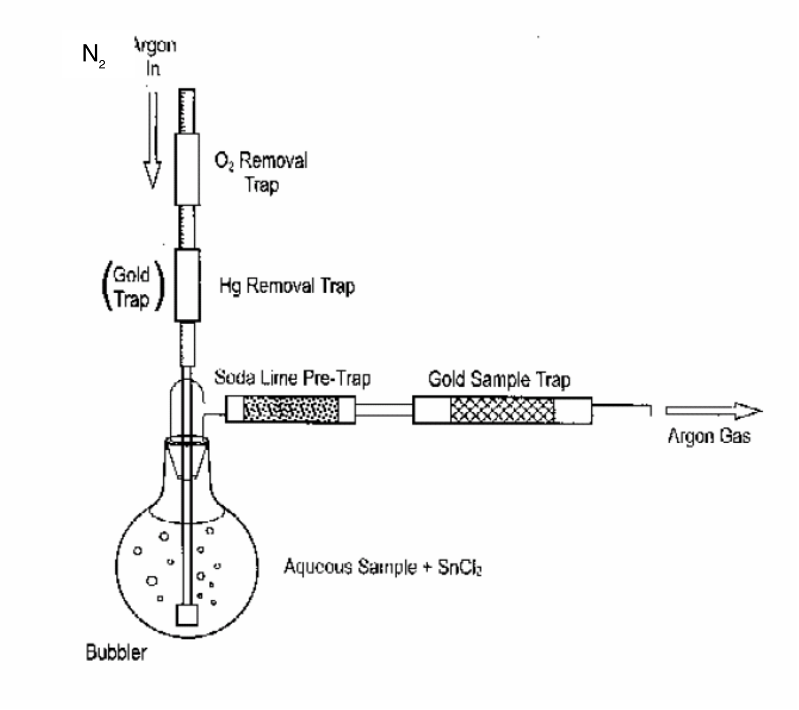

Figure 324-3.
Schematic of the bubbler system

11.5 *Desorption of Hg from the gold trap, and peak evaluation.*

11.5.1 Remove the sample trap from the bubbler, place the nichrome wire coil around the trap and connect the trap into the analyzer train between the incoming Hg-free argon and the second gold-coated (analytical) sand trap (Figure 324-2)

11.5.2 Although not required, it may help to pass argon through the sample and analytical traps at a flow rate of approximately 30 mL/min for 2 min to drive off condensed water vapor.

11.5.3 Apply power to the coil around the sample trap for 2 minutes to thermally desorb the Hg (as Hg^0) from the sample trap onto the analytical trap.

11.5.4 After the 2 minute desorption time, turn off the power to the nichrome coil, and cool the sample trap using the cooling fan.

11.5.5 Turn on the chart recorder or other data acquisition device to start data collection, and apply power to the nichrome wire coil around the analytical trap. Heat the analytical trap for 1.5 minutes.

11.5.6 Stop data collection, turn off the power to the nichrome coil, and cool the analytical trap to room temperature using the cooling fan.

11.5.7 Place the next sample trap in line and proceed with analysis of the next sample. *NOTE: Do not heat a sample trap while the analytical trap is still warm; otherwise, the analyte may be lost by passing immediately through the analytical trap*.

11.5.8 Peaks generated using this technique should be very sharp and almost symmetrical. Mercury elutes at approximately 1 minute and has a width at half-height of about 5 seconds.

11.5.8.1 Broad or asymmetrical peaks indicate a problem with the desorption train, such as improper gas flow rate, water vapor on the traps(s), or an analytical trap damaged by chemical fumes or overheating.

11.5.8.2 Damage to an analytical trap is also indicated by a sharp peak, followed by a small broad peak.

11.5.8.3 If the analytical trap has been damaged, the trap and the fluoropolymer tubing downstream from it should be discarded because of the possibility of gold migration onto downstream surfaces.

11.5.8.4 Gold-coated sand traps should be tracked by unique identifiers so that any trap producing poor results can be quickly recognized and discarded.

11.6 *Instrument Calibration.* Analyze the standards by CVAFS following the guidelines specified by the instrument manufacturer. Construct a calibration curve by plotting the absorbance of the standards versus g/l Hg. The R^2 for the calibration curve should be 0.99 or better (R = 0.995). If the curve does not have an R^2 value equal to or better than 0.99 then the curve should be rerun. If the curve still does not meet the criteria then new standards should be prepared and the instrument recalibrated. All calibration points contained in the curve must be within 10 percent of the calibration value when the calibration curve is applied to the calibration standards.

11.7 *Sample Analysis.* Analyze the samples following the same procedures used for instrument calibration. From the calibration curve, determine sample Hg concentrations. To determine total Hg mass in each sample fraction, refer to calculations in Section 12. Record all sample dilutions.

11.8 *Continued Calibration Performance.* To verify continued calibration performance, a continuing calibration check standard must be run every 10 analytical burn cycles. The measured Hg concentration of the continuing calibration check standard must be within 20 percent of the expected value.

11.9 *Measurement Precision.* The QA/QC for the analytical portion of this method is that is that one sample per digest or 1 out of every 10 samples, whichever is greater, is to be analyzed in duplicate. The duplicate results must be within 20% RPD of each other.

11.10 *Measurement Accuracy.* Immediately following calibration, an independently prepared standard (Section 7.7.5) must be analyzed. This standard is called the Initial Calibration Verification (ICV) and must recover between 80-120% of the expected value. In addition, for every digestion or per 10 samples, whichever is greater, a know addition pair is performed called an analytical spike and analytical spike duplicate (AS/ASD). The AS/ASD is a measure of the matrix effect within the spiked samples must be recovered between 75-125% of the expected value.

11.11 *Independent QA/QC Checks.* It is suggested that the QA/QC procedures developed for a test program include submitting, on occasion, spiked Hg samples to the analytical laboratory by either the prime contractor, if different from the laboratory, or an independent organization. The measured Hg content of reference samples must be within 15 percent of the expected value. If this limit is exceeded, corrective action (*e.g.,* re-calibration) must be taken and the samples re-analyzed.

11.12 *Quality Assurance/Quality Control.* For this method, it is important that both the sampling team and analytical people be very well trained in the procedures. This is a complicated method that requires a high-level of sampling and analytical experience. For the sampling portion of the QA/QC procedure field blanks are required. It should be noted that if high-quality reagents are used and care is taken in their preparation and in the train assembly, there should negligible, if any, Hg measured in the field blanks.

11.13 *Field Blanks.* A field blank is performed by assembling a sample train, transporting it to the sampling location during the sampling period, and recovering it as a regular sample. These data are used to ensure that there is no contamination as a result of the sampling activities. A minimum of one field blank at each sampling location must be completed for each test site. Any Hg detected in the field blanks cannot be subtracted from the results. Whether or not the Hg detected in the field blanks is significant is determined based on the QA/ QC procedures established prior to the testing. At a minimum, if field blanks exceed 30 percent of the measured value at the corresponding location, the data must be flagged as suspect.

12 Calculations and Data Analysis.

12.1 Mercury concentrations are typically calculated on a g/trap basis using the equation listed below.

12.2 Calculate the Hg concentration of each digested sample in g/digest according to the following equation:

$$[Hg/Digest]\ (\ g/digest) = [(A_A - A_{BB})/CF_M]/V_{ALI} * V_{DIG}$$

where:
A_A = peak height (or area) for Hg in the sample aliquot
A_{BB} = mean peak height (or area) for Hg in the calibration blanks
CF_M = slope or mean calibration factor
V_{ALI} = volume of aliquot used for analysis
V_{DIG} = volume of digestion

12.3 Calculate the reagent blank corrected concentration of each digested sample and the overall trap concentration using the following equations:

$$[\mathrm{Hg/Digest}]_{RB}\ (\ \mathrm{g/digest}) = [\mathrm{Hg/Digest}] - RB_{AVE}$$

$$[\mathrm{Hg/Trap}]\ (\ \mathrm{g/trap}) = A[\mathrm{Hg/Digest}]_{RB} + B[\mathrm{Hg/Digest}]_{RB}$$

where:

RB_{AVE} = average reagent blank in g/digest as calculated in 12.2
$A[\mathrm{Hg/Digest}]_{RB}$ = A Section digest concentration, reagent blank corrected
$B[\mathrm{Hg/Digest}]_{RB}$ = B Section digest concentration, reagent blank corrected

12.4 If a correction for sorbent blank material is desired (as discussed in 9.2) use the following equation, if not proceed to section 12.5:

$$[\mathrm{Hg/Trap}]_{SB} = [\mathrm{Hg/Trap}] - SB_{AVE}$$

where:
SB_{AVE} = average sorbent blank in g/digest as calculated in 12.3

12.5 Using the gas volume that was collected on the sorbent trap during sampling, the mercury concentration in fluegas is calculated using the following equation:

12.6

$$\mathbf{[Hg]\ (\ g/m^3) =} [\mathrm{Hg/Trap}]/\mathbf{V_{GAS}}$$

or

$$\mathbf{[Hg]\ (\ g/m^3) =} [\mathrm{Hg/Trap}]_{SB}/\mathbf{V_{GAS}}$$

where:
V_{GAS} = volume of gas (flue gas) collected on trap in units of dry standard cubic meters (dscm)
$[\mathrm{Hg/Trap}]$ = mercury collected on trap as calculated in 12.3
$[\mathrm{Hg/Trap}]_{SB}$ = sorbent blank corrected mercury collected on trap as calculated in 12.4

12.7 The mercury emission rate in lb_{Hg}/TBtu is calculated as described in the complete EPA Method-324.

13 *Constant Proportion Sampling.* See complete EPA Method-324 document

14 *Sampling and Data Summary Calculations.* Refer to 40 CFR Part 60, appendix A. Methods 2, 4, 5, and 19 for example calculations.

15 *Pollution Prevention.*

15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operation. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address waste generation. When it is not feasible to reduce wastes at the source, the Agency recommends recycling as the next best option. The acids used in this Method should be reused as practicable by purifying by electrochemical techniques. Glass tube from the sorbent trap and other chemicals used in this Method are the neat materials used in preparing standards. These standards are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards.

15.2 For information about pollution prevention that may be applied to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Governmental Relations and Science Policy, 1155 16th Street NW, Washington DC 20036.

16 Waste Management

16.1 The laboratory is responsible for complying with all Federal, State, and local regulations governing waste management, particularly hazardous waste identification rules and land disposal restrictions, and for protecting the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required. An overview of requirements can be found in *Environmental Management Guide for Small Laboratories* (EPA 233-B-98-001).

16.2 Acids, samples at pH <2, and BrCl solutions must be neutralized before being disposed of, or must be handled as hazardous waste.

16.3 For further information on waste management, consult The *Waste Management Manual for Laboratory Personnel* and *Less is Better: Laboratory Chemical Management for Waste Reduction*, both available from the American Chemical Society's Department of Government Relations and Sciences Policy, 1155 16th Street NW, Washington, DC 20036.

17 Bibliography.

17.1 EPA Method 1631, Revision E "Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry," August 2002.

17.2 "Comparison of Sampling Methods to Determine Total and Speciated Mercury in Flue Gas," CRADA F00–038 Final Report, DOE/NETL–2001/1147, January 4, 2001.

17.3 CFR part 60, appendix A, "Method 29—Determination of Metals Emissions from Stationary Sources."

17.4 1CFR part 60, appendix B, "Performance Specification 12A, Specification and Test Procedures for Total Vapor Phase Mercury Continuous Emission Monitoring Systems in Stationary Sources."

17.5 ASTM Method D6784–02, "Standard Test Method for Elemental, Oxidized, Particle-bound and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method)."

17.6 Bloom, N. S.; Fitzgerald, W. F. "Determination of Volatile Mercury Species at the Picogram Level by Low-Temperature Gas Chromatography with Cold-Vapor Atomic Fluorescence Detection," *Anal. Chim. Acta*. 1988, 208, 151.

17.7 Bloom, N. S. "Trace Metals & Ultra-Clean Sample Handling," *Environ. Lab*. 1995, 7, 20.

18 Glossary

18.1 **A Section** –The first (front) portion of the sorbent trap on which the majority of the mercury sample is captured

18.2 **B Section** – The second (back) portion of the sorbent trap used to evaluate mercury breakthrough and sample collection quality. Appendix K refers to this as Section 2.

18.3 **FSTM** – Fluegas Sorbent Total Mercury, the sorbent trap that has passed EPA Method 301 Validation.

18.4 **May** --This action, activity, or procedural step is allowed but not required.

18.5 **May not** --This action, activity, or procedural step is prohibited.

18.6 **Laboratory Matrix Spike (LMS) and Matrix Spike Duplicates (MSD)**—Aliquots of an environmental sample to which know quantities of the analyte of interest is added in the laboratory. The LMS and MSD are analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LMS and MSD corrected for these background concentrations.

18.7 **Must** –This action, activity, or procedural step is required.

18.8 **Reagent Blanks**--Solution blanks are used to determine the concentration of mercury in the reagents that are used to prepare and analyze the samples. In this Method, reagent blanks are required when each new batch of solutions is prepared.

18.9 **Reporting Limit** – The minimum reportable quantity.

18.10 **Sorbent Trap** – The glass tube packed with chemically-treated charcoal for the capture of mercury and includes both the A and B sections.

18.11 **Sorbent Trap Field Blank** –Sorbent traps that are taken to the sampling site and exposed to the same equipment and handling as a sampled trap, except that no flue gas is drawn through the trap. The field blank is used to demonstrate that samples have not been contaminated by the sampling and handling protocol.

18.12 **Sorbent Trap Lab Blank**—A sorbent trap withdrawn from a batch or lot of sorbent traps and analyzed to demonstrate that the sorbent traps have not been contaminated during the manufacturing and packaging process.

18.13 **Shall** – This action, activity, or procedure is required.

APPENDIX A

COMMENTARY ON MODIFICATIONS OF METHOD-324

The optimization of this sorbent trap method for mercury measurement occurred over a period of more than thirteen years, and many lessons were learned along the way. Although it is critical that the method is flexible enough to allow for changes in the way that various activities are performed (such as allowing an alternative type of laboratory analysis or digestion/extraction), these changes to the validated approach should in themselves undergo validation prior to acceptance. The critical areas that need to be performed in the same way as the validated tests are:

- Sorbent traps – the traps that have been successful have very stringent quality control as reflected in blank levels (absolute mercury level and variability) and breakthrough levels.
- Clean handling – the traps need to be handled with clean gloves, enclosed in clean containers, and sealed off after testing. Throughout the handling of the sample trap, from production through sampling and analysis, clean handling is essential.
- Sorbent traps need to be inserted directly in the flue gas duct when sampling, with no upstream tubing, filter, etc. If any upstream tubing, filters or other materials are used prior to the traps, they must be prepared under clean conditions and proven to avoid gaseous mercury losses.
- The sorbent traps must have a front and back section, such that breakthrough to the back section can be quantified.
- Condensation or wetting must not occur in the sample trap.
- The sample flow rate and total volumes sampled are based on the specific trap designs tested.
- Sample volume must be accurately measured.
- Digestion as specified in the draft method is the only approach that is proven through Method 301 validation.
- Small aliquots must be used in the analysis in order to obtain the low detection levels without matrix interference.
- It is necessary to purge and trap or preconcentrate the sample.
- CVAFS is the only analytical technique currently proven for this matrix.

The Quick SEM™ Method on which Method 324 is based and validated was done with cold vapor atomic fluorescence spectrometry (CVAFS) analysis. Therefore, the minimum sample times and flow rates are based on collecting sufficient Hg to obtain the required detection limits necessary for flue gas measurements. It will be necessary to adjust these values if a less sensitive analytical procedure, such as cold vapor atomic absorption spectrometry (CVAAS), if used. Digestion is also a key step. All the work to date on Quick SEM™ has used one technique for digesting/extracting Hg from the trap. While other digestion/extraction techniques may be acceptable, no supporting data has yet been developed.

A.3 Modified ASTM Method D 6414

Determination of Total Mercury in Iodide-Promoted Activated Carbon Sorbent Tubes by Acid Extraction/Cold Vapor Atomic Absorption or Atomic Fluorescence Spectroscopy

1. Summary of Method

Mercury in the iodide-treated activated carbon material is extracted by heating the test sample at a specified temperature in a mixture of nitric and hydrochloric acids. The acid solutions produced are transferred into a vessel in which the mercury is reduced to elemental mercury. The mercury vapor is determined by cold-vapor atomic absorption or atomic fluorescence spectrometry.

NOTE 1—Mercury and mercury salts can be volatilized at low temperatures. Precautions against inadvertent mercury loss should be taken when using this method.

2. Apparatus Needed

2.1 *Analytical Balance.* The balance must have a sensitivity of 0.1 mg.
2.2 *Atomic Absorption or Atomic Fluorescence Spectrometer.* The system must have a cold-vapor mercury analysis system.
2.3 *Digestion Vessels*. These vessels can be 50-to 250-mL bottles with an efficient seal and screw cap. The bottles must be compatible for use with aqua regia. Glass, polycarbonate and HDPE bottles are acceptable. The bottles and cap assemblies shall be washed in 6 M HCl and dried before each use.

NOTE 2—Other bottle and cap assemblies may be used provided they are compatible for use with aqua regia at a temperature of 80°C.

2.4 *Heat Source.* A uniform heating block, or a water bath capable of maintaining a constant temperature of 80°C is to be used.
2.5 *Syringe and Filter*. The syringe should be large (i.e., 20-cm^3) with a 1-μm PTFE filter to fit the syringe.

3. Sample

Prepare the sample in accordance with the instructions distributed with the sorbent tubes for cutting the tubes and transferring the sample and glass fiber plugs to the digestion vessels.

4. Reagents

Use the procedures in Section 8 of ASTM Standard Test Method D 6414 (2) for the reagents needed.

5. Procedure

5.1 *Preparation of Test Solution (Extraction Step):*

5.1.1 Weigh the test portion transferred from the sorbent tube into a digestion bottle. Record the weight (W_s) to the nearest 0.0001 g.

5.1.2 There are two acid extraction solutions that may be used, aqua regia and 50:50 hydrochloric:nitric acids. In both cases the hydrochloric acid should be added to the sorbent material first to minimize the release of nitrogen oxides.

5.1.2.1 Aqua Regia—Quantitatively add concentrated hydrochloric and nitric acids, at the rate of 6 mL of concentrated hydrochloric acid and 2 mL of concentrated nitric acid per gram of sorbent material, to the digestion bottle and secure the cap. Add the hydrochloric acid to the sorbent material first.

5.1.2.2 A 50:50 hydrochloric:nitric acid mixture—Quantitatively add concentrated hydrochloric and nitric acids, at the rate of 7.5 mL of concentrated hydrochloric acid and 7.5 mL of concentrated nitric acid per gram of sorbent material, to the digestion bottle and secure the cap (Note 4). Add the hydrochloric acid to the sorbent material first.

NOTE 4—The amount of 50:50 hydrochloric:nitric acids used depends on the individual laboratory. During the course of the study, some labs used 4 mL of concentrated hydrochloric acid and 4 mL of concentrated nitric acid per gram of sorbent material. A lab that used 7.5 mL of concentrated hydrochloric acid and 7.5 mL of concentrated nitric acid per gram of sorbent material got better recoveries and more precise results.. It is recommended that labs use the higher amounts of acid for extractions, i.e., 30 mL of 50:50 hydrochloric:nitric acids in a 50 mL vessel for 2 g of sorbent material.

5.1.3 Transfer the digestion bottle and contents to a heating block preheated 80°C and heat the digestion vessels for one hour. If a water bath is used , preheat the bath to 80°C and heat for 1 hour. Secure the digestion bottle in such a way as to keep the contents below the surface of the water.

5.1.4 After heating, remove the digestion bottle from the heat source and allow to cool to room temperature.

NOTE 5—**Caution**: Be sure the digestion vessels are at room temperature before removing the cap. Carefully relieve the pressure by slowly removing the cap.

5.1.5 Quantitatively add sufficient water so that the final volume of the mixture, after adding all reagents, will be 50 mL and mix the contents. The amount of water needed is 14.5 mL if 30 mL of acid is used for a 2 g sorbent sample. This amount is to be adjusted if a different volume of acid is used.

5.1.6 Add 5 mL of 5 % potassium permanganate solution and mix thoroughly. Allow the mixture to stand for 10 min.

5.1.7 Add 0.5 mL of the hydroxylamine sodium chloride solution and mix. If a pink color persists for more than 1 min, add an additional 0.5 mL of the hydroxylamine sodium chloride solution and mix. Note the total volume, if more than one 0.5 mL increment of hydroxylamine hydrochloride solution is added, and record this volume (V) for use in the final calculations.

5.1.8 *Test Solution Filtering* —It is very important that as soon as all the reagents have been added the extract solution should be filtered to remove the suspended carbon (NOTE 6).

5.1.8.1 Using the large (i.e. 20-cm^3) syringe, draw the Test Solution into the syringe.

5.1.8.2 Fit the syringe with a 1-µm filter and deliver the filtered solution to a clean, acid-washed holding vessel. The volume of the test solution is known (V) so it is not necessary to use volumetric holding vessels.

5.1.8.3 Repeat steps 5.1.8.1 and 5.1.8.2 to recover as much of the remaining Test Solution as needed.

NOTE 6—Carbon must be removed from the Test Solution to prevent the reabsorption of mercury, especially as the acid strength of the solution is lowered upon dilution. The filtering process should be completed as soon as possible after the preparation of the solution. Other filtering processes may be used, i.e., filter paper and funnels, as long as the analyst ensures all the materials used are mercury free. Not all of the test solution needs to be recovered, just enough to complete the analyses and rechecks.

5.2 *Preparation of Reagent Blank*—Prepare a reagent blank by repeating the procedure in 5.1 but without the sample.

5.3 *Preparation of Quality Control Sample:*

5.3.1 Prepare a test portion of a certified reference material (CRM) for analysis using the procedure described in 5.1.

5.3.1.1 Use a portion of iodated (iodized) activated carbon blank as the solid material. Weigh the solid material (use approximately the same mass as the test samples) in a digestion vessel.

5.3.1.2 Add a small amount of a mercury solution with a certified known concentration (i.e., NIST 1641d). The solution can be added with a calibrated micropipette, but the mass of solution added must be measured (W_{CRM}).

5.4 *Atomic Absorption/Atomic Fluorescence Analyses:*

5.4.1 *Instrument Conditions*—Follow the instrument manufacturer's recommended procedure for optimizing the performance of the instrument and the cold-vapor apparatus (NOTE 7).

NOTE 7—There are two basic types of atomic absorption and atomic fluorescence spectrometers. One type of spectrometer uses a fixed reduction cell to which specific amounts of test solution and reducing solutions are mixed. All the mercury vapor produced during the analysis is measured by measuring total absorbance (or fluorescence) *vs*. time and the total signal integrated. The second type of spectrometer introduces a specific concentration of reductant and the test solution through a flow injection system and a reactant cell that mixes the reactants. The solutions are carefully metered with peristaltic pumps. The concentration of mercury in the test solution is measured by the mercury released and measured constantly during the steady state operation of the system.

5.4.2 *Instrument Calibration:*

5.4.2.1 Prepare 50 mL of 0.5, 1, 3, 5, and 10 ng/mL (ppb) of mercury calibration standards in a HCl:HNO_3 solution (NOTE 8) by serial dilution of the 100 ng/mL mercury standard solution. All mercury solutions are to be prepared daily.

NOTE 8—The calibration solutions must have the same acid concentrations as the test solution. Use the same concentrations of HCl and HNO_3 as that in the final volume of the Test Solution to prepare the calibrating solutions.

5.4.2.2 Follow the instrument manufacturer's recommendations for adding the calibration solutions to the reduction flask or reduction system.

5.4.2.3 In the analysis of the calibration solutions enough stannous chloride solution should be added to ensure complete reduction of the mercury in the calibration solution.

5.4.2.4 Record the absorbance of each calibration standard.

5.4.3 *Analysis of Test Solution:*

5.4.3.1 Determine the absorbance (A_s) of the Test Solution using the procedure described in 5.4.2.

5.4.3.2 Using the HCl:HNO_3 matrix matching solution, dilute test solutions with mercury absorbances greater than the highest calibration standard to give an estimated absorbance equivalent to the 3-ng/mL calibration standard and reanalyze (NOTE 9).

NOTE 9—The test solution extract contains a combination of iodide, I^-, and molecular iodine, I_2, which together form the colorless complex ion I_3^-. The promoted activated carbon sorbent contains iodide that is oxidized to molecular iodine by the nitrate ion in the extraction process. Iodine and the complex ion I_3^- both oxidize stannous chloride, with the result that larger amounts of stannous chloride are needed to first reduce molecular iodine and the complex ion I_3^- before reacting with the mercury in the test solution. Extensive dilution (by 50 or more) of the extract solution is recommended to minimize these interferences in the analysis process.

5.4.3.3 Record the dilution factor as DF.

5.4.4 *Analysis of the Reagent Blank*—Determine the absorbance (A_b) of the reagent blank using the procedure described in 5.4.2.

5.4.5 *Analysis of the Quality Control Sample*—Determine the absorbance (A_{qcs}) of the quality control sample using the procedure described in 5.4.2.

6. Calculations

6.1 The following calculations are applicable to both the *Test* Samples and *Quality Control Sample:*

6.1.1 Prepare a calibration curve by plotting absorbances of calibration standards minus the absorbance of the reagent blank (properly corrected for dilution) versus the concentrations of the calibration solutions in ng/mL. It is recommended that **only** a linear fit of the form $y = mx + b$ be used for the calibration plot analysis.

6.1.1.1 Calculate the net absorbance for each of the Test Samples and quality control sample as follows

$A_{net} = A - A_b$

where:

A = absorbance of the test sample (A_s) or quality control sample (A_{qcs}), and

A_b = absorbance of the reagent blank (corrected for dilution).

6.1.1.2 Read the concentration of the test samples, C_s, and the quality control sample, C_{qcs}, from the calibration curve.

6.1.1.3 Calculate the amount of mercury, in ng, in the test samples and quality control sample as follows

$$\text{Mercury (ng)} = DF \times V \times C \qquad (1)$$

where:

C = the concentration of the test sample, C_s, and the quality control sample, C_{qcs}, read from the calibration plot, ng/mL;

DF = is the dilution factor,

V = volume of the analysis solution in mL.

6.1.1.4 Calculate the mercury recovery from th equality control sample as follows

$$\text{Mercury recovery} = (\text{ng mercury})/\text{CRME} \times 100$$

where:

ng mercury = the mercury value of the sample calculated by Equation (1)

CRME = the expected value in ng of mercury in the quality control sample.

7. Report

7.1 Report the results of the mercury analysis on a total nanogram basis.

7.2 Report the recovery of mercury in the quality control sample.

7.3 Report the digestion acid used.

A.4 Application of Thermal Desorption/AAS to Sorbent Tube Analysis

The following considerations will assist users of thermal desorption analyzers to obtain optimal results from sorbent tube mercury analysis:

Laboratory Preparation for Analysis

1. Clean the bench top where analysis is to be performed with an acid-containing detergent such as Citranox.
2. Cover the bench top with a clean sheet of aluminum foil. This will allow any spilled carbon particles to be easily recovered.

Carbon Tube Preparation

1. Before opening the tube, clean the outside with methanol to remove any potential contaminants. This is especially important when analyzing tubes sampled from a flue gas with high particulate content.
2. Remove any static from the carbon particles by passing the tube over an antistatic material such as polonium. Po-210 is commercially available and is commonly used in laboratories that perform XRF analyses. Removing the static greatly diminishes the chances of losing carbon particles. Often the carbon particles in tubes used to sample flue gas carry a static charge, causing the particles to move around.
3. Use a cutting tool to open the tube to reduce the risk of losing carbon particles. Metal snips may also be used but the risk of losing particles is much greater.
4. Cut the tube just above the glass wool plug in front of the first (A) section.
5. Carefully remove the glass wool using a dental pick (or similar instrument) and set the wool aside on a piece of aluminum foil. The wool will be analyzed later.
6. Carefully transfer the carbon particles to the sample ladle. It is very important to perform the transfer over a clean piece of aluminum foil so that any spilled particles can be easily recovered.
7. Cover the carbon particles with a thin layer of sodium carbonate. Any sodium carbonate that is above the edge of the ladle must be removed. If the excess sodium carbonate is not removed, it will spill over inside the desorption furnace and will eventually cause the instrument to malfunction. The sample is now ready to analyze.
8. Wrap the glass wool in aluminum foil and place in the ladle. Cover completely with sodium carbonate. This sample is now ready to analyze.

Instrument Preparation

1. Ensure that the lenses are clean before heating up the furnace. This can be checked by looking at the PMT line, which should be above 16,000. In general, the lenses should be cleaned after every 100 analyses
2. The current RP-M324 thermal attachment has four temperature ramp profiles controlled by a WATLOW temperature controller. It is critical for accurate measurement that the analyst select the appropriate temperature profile according to the expected mass of Hg on the sample(s). The typical mass ranges for each profile are: 1) 10 – 2,000 ng, 2) 100 – 20,000 ng, 3) 500 – 50,000 ng, and 4) 500 – 100,000 ng. All samples with an expected loading of less than 2,000 ng should be analyzed using profile #1. For samples with loadings between 2,000 and 20,000 ng ramp profile #2 should be used. The analysis for samples in this range can be further improved by changing the temperature setting within profile #2. For example if the expected sample loading is less than 10,000 ng then it is recommended to change the starting temperature in profile #2 from 400°C to 480°C. This decreases the time of analysis and allows the analyst to build a calibration curve that is more linear throughout the dynamic range. It has been observed that the R^2 for calibration curves generated with the modified temperature profile is better than the R^2 for calibration curves without any modification to the temperature profile. Samples with

expected mass loadings greater than 20,000 ng should be analyzed using either profile #3 or #4.

3. After selecting the appropriate temperature profile the furnace should be allowed to warm up for a minimum of 2 hours prior to analysis.
4. Prior to performing analyses the furnace should be “steam cleaned”. This is performed by placing approximately 1 ml of water in a sample ladle and introducing the ladle into the furnace. This technique greatly improves analysis of low-mercury containing samples. If at any time the analyst notices that the RSD is greater than 10% this steam cleaning technique should be performed. If this technique does not reduce the RSD below 10% then the lenses must be cleaned.

Calibration

5. When calibrating the instrument the same carbon mass and type as is in the samples must be used. This is particularly true when analyzing iodated carbon, due to the interference from the iodine.
6. It is highly recommended that liquid mercury standards are used to generate the calibration curve. The standard should be at the appropriate concentration such that less than 200 μl of standard is “spiked” onto the carbon. Too much liquid may cause erroneous results, as water can act as an interferent.
7. A calibration curve should be generated that covers an appropriate range. For example, if the expected mass of mercury on the samples is around 100 ng, then the curve should be from 20 to 500 ng. You would not want to use a curve ranging from 20 to 10,000 ng. If the expected mass of mercury on the samples is around 7,000 ng, then the curve should range from 1,000 to10,000 ng. This is an important point because all AAS systems are not linear throughout their dynamic range.

A.5 Direct Combustion Analysis/AAS

Sorbent Tube Sample Preparation and Analysis for Mercury

Used with permission of LECO Corporation

Equipment:

- Spex Mill 8000M® mixer/mill
- Spex mixing vial, 2 •” diameter X 3” vial body with screw on cap and O-ring
- Spex mix/mill balls, three ¼” steel balls
- AMA254 Mercury Analyzer

Procedure:

1. The sorbent tube is opened and total weight of the carbon in both sections is determined and recorded. Section A is the analytical portion of the tube and section B is used to check for analyte break-through.
2. The front portion of section B is analyzed without grinding to check for analyte break-through. Only one analysis is made on this section unless the result is greater than five times the average blank measurement on the AMA254, in which case, a second determination is performed to confirm the result. Such a result would be indicative of analyte break-through and any results from the analytical portion (section A) are suspect.
3. Section A is divided into two relatively equal portions.
4. Each portion of section A is ground separately in a ball mill.[1] Place a portion of section A into the mixing vial with three ¼" steel balls and screw the mixing vial lid on securely.
5. Place the mixing vial into the vial holder within the mixing mill and tighten the vial restraint.
6. Set the timer on the mill for two minutes. After the first two minutes of grinding allow the vial to sit for one minute.[2] Then set the timer for an additional two minutes of grinding.
7. Remove the mixing vial, unscrew the cap and remove the ground sample and mixing balls.
8. The other portion of Section A is also ground following steps 4 – 7.
9. The two ground portions of section A are then combined and thoroughly mixed by placing them together into the mixing vial with three ¼" steel balls and screw the mixing vial lid on securely.
10. Place the mixing vial into the vial holder within the mixing mill and tighten the vial restraint.
11. Set the timer on the mill for one minute.
12. Remove the mixing vial, unscrew the cap and remove the ground sample and mixing balls.[3]
13. The total ground section A is weighed and recorded and sample loss from grinding is determined.[4]
14. Three determinations are then made on this ground and mixed material from section A. If the deviation of these three replicates is high, additional runs are added.[5]

[1] Section A is split to avoid overloading the mixer mill.

[2] The one minute delay is used to keep the mill and material cool to avoid the possibility of analyte loss.

[3] The mixing vial and balls are rinsed with ethanol between analyses.

[4] The sample loss observed for this sample handling and grinding step has been determined to be ~4% with a maximum loss of <8%.

[5] The calculated RSD of this procedure is 5%. In many cases it is better than 2%.

A.6 Phase II Round Robin Instructions to Participants

Memorandum

Date: June 2, 2006

TO: EPRI Sorbent Tube Mercury Analysis Round Robin Study Participants

FROM: Naomi Goodman, EPRI

SUBJECT: Instructions for Phase II – Round Robin Study

Enclosed are samples for Phase II of EPRI's Sorbent Tube Mercury Analysis Round Robin project. The following materials are provided in this shipment:

30 – spiked sorbent tubes (spiked in the range of ~50 to ~50,000 ng/tube)
2 – unspiked tubes for use as a quality control sample
1 – inventory of tube numbers included in your shipment

Please compare the tube numbers in your shipment with the inventory and send an email to Rob Keeney (keeney.rob@epamail.epa.gov) within 24 hours of receipt confirming that there are no missing tubes.

The deadline for submitting your results from Phase II is July 7, 2006. Results should be transmitted to Dr. Riley in an Excel spreadsheet. Include the tube number with each result. Include your calibration levels and results as well as blank results in your report.

The purpose of Phase II is to determine the precision and bias of all analytical methods, on samples of unknown concentration, using the procedures developed during Phase I. Attachment 1 to this memo lists laboratory procedures that we are requesting you to follow if you are using wet chemistry methods (Draft Method 324 and modified ASTM 6414). Labs using thermal desorption or direct combustion methods should contact Dr. Riley for instructions.

The verified spike loadings will not be revealed to participants until after all results are received. If you anticipate any difficulty with calibrating for the range of sample concentrations, please contact John Riley to discuss an approach for your specific instrument. The lowest spike level will not be detectable on most atomic absorption instruments, so failure to detect a signal does not mean that the tube was not spiked. The low level spikes are included in the study to assist those companies that are equipped to analyze short-duration (RATA) samples in their own laboratories.

As part of the Phase II study, we are requesting each lab to prepare and analyze one quality control sample spiked with a known quantity of mercury. The results of this sample will provide critical information that we need to investigate an apparent low bias of wet chemistry methods versus the thermal desorption and direct combustion methods. We have included in this shipment two unspiked sorbent tubes to perform this test. You will also receive an ampoule of NIST SRM mercury solution in a separate package. Attachment 2 provides a procedure for spiking the sorbent material.

Dr. Riley has suggested an improvement to the calibration method for wet chemistry methods that should improve the accuracy of these methods. Attachment 3 details this sample addition method. Use of this approach is not mandatory, but I encourage you to consider using it for the Phase II study.

Please contact Dr. Riley if you have any specific questions regarding the Phase II instructions. .

Naomi Goodman, Project Manager

Enclosure:

Phase II sorbent tube study materials

Attachment:

1. Instructions and Notes for Analysis – Phase II
2. Instructions for Quality Control Sample
3. Sample Addition Procedure

EPRI Sorbent Tube Mercury Analysis
Instructions and Notes for Analysis – Phase II

From John T. Riley

Following are some instructions and notes about the analysis and reporting of the Phase II samples. Please be sure this information is conveyed to everyone involved in the analysis, especially appropriate lab personnel.

1. Each participating laboratory should establish a plan for the analysis of the samples so that the analysis reports are completed by the due date.

2. Each laboratory should try to complete the analyses in no more than three batches.

3. Following are some laboratory procedures that should be followed:

   - All weighings are to be made to the nearest 0.1 mg on an analytical balance.
   - All additions of liquids in the extraction stage are to be done with class A volumetric glassware or properly calibrated automatic pipetting systems.
   - All diluting should be done with class A volumetric glassware.
   - Both sections (A and B) of the sorbent tube are to be analyzed, as well as the glass wool separating them.

4. All participating laboratories should follow the appropriate procedures and guidelines (especially the extraction procedures in Draft Method 324 and Draft Modified ASTM Method D 6414) as closely as possible.

5. The participating laboratories are requested to report **only the raw data from the analyses, not corrected data. All laboratories are requested to report:**

   - All calibration data and standards used
   - Data from all sample runs (including multiple runs of the extract solutions)
   - All reagent blank data
   - All quality control sample analysis data

EPRI Sorbent Tube Mercury Analysis – Phase II
Notes for Quality Control Sample
For Participants using Draft Method 324 and Draft Modified ASTM Method 6414

From John T. Riley

Note: Labs using thermal desorption or direct combustion methods should contact John T. Riley for specific instructions. Email – bgrileys@insightbb.com; phone – (270) 842-2757; cell phone – (270) 791-5055.

Laboratories using wet chemistry methods should use the following procedure to prepare and analyze a Quality Control sample (spiked Matrix Blank) for Phase II. Please be sure this information is conveyed to everyone involved in the Phase II analysis, especially appropriate lab personnel.

1. Each participating laboratory has been provided with two blank sorbent tubes that are to be used to prepare matrix spike samples. The promoted activated carbon in the A section of the two tubes will be used as the matrix for the Quality Control samples.

2. Each participating laboratory will receive an ampoule of NIST 1641d, a standard reference material, which is to be used to spike the promoted activated carbon.

3. All of the promoted activated carbon from section A of one sorbent tube is to be placed in the extraction vessel and weighed. A 500 µL portion of 1641d is pipetted onto the carbon in the extraction vessel and the vessel is reweighed to calculate the exact mass of 1641d added. This amount of 1641d will add 795 nanograms of mercury to the activated carbon.

4. The quality control samples are to be analyzed using the exact same procedure as the extract samples.

5. Report the nanograms of mercury recovered in the quality control sample. **Do not correct the values for any reagent blanks.**

EPRI Sorbent Tube Mercury Analysis
Proposed Sample Addition Procedure
From John T. Riley

The following procedure may be used to determine the sample dilution giving the minimum interference from the molecular iodine present in the extract solutions from Draft Method 324 and Draft Modified ASTM Method D 6414.

1. This procedure only needs to be performed on one sample extract, provided the same extraction procedure is used for all samples.

2. Determine by your own in-lab measurements, or from the instrument manufacturer, the most sensitive working range for the spectrometer you use. This will not be a wide range of concentrations of several orders of magnitude, but a narrow range, usually around 0-10 ppb.

3. Choose one of the extract solutions, preferably one of the lower concentrations, i.e., in the 300-1000 ng range. The selection of the extract solution should be done after initial screening of the extracts, which every laboratory does to determine if the extract's measured absorbance falls within the limits of their calibration plot.

4. Prepare a calibration curve for the most sensitive region using 4 to 5 calibration standards, e.g.., 0.5, 1.0, 3.0, 5.0, and 10.0 ppb.

5. Using a mid-range calibration standard, e.g.., 3 .0 ppb, prepare a series of solutions by using a fixed volume of the calibrating solution and add successively smaller increments of the extract solution. For example;

   - To 20 mL of the calibration standard add 2.0 mL, 1.0 mL, 0.50 mL, 0.20 mL, 0.10 mL, and 0.050 mL.
   - The dilutions calculated after making these additions to 20.0 mL are 11, 21, 41, 101, 201, and 401.

6. Calculations of the changes in solution Absorbance per increment of extract volume can be made by the equation:

   Change in Absorbance =
   {(Absorbance measured for mixture) – [(Absorbance of calibration standard)*(volume of calibration standard)/(total volume of calibration standard + increment of extract)]}/{volume of extract increment used}

When the change in absorbance per increment reaches a constant (99%), the chemical interference from the molecular iodine should be negligible. The dilution factor that produces this level of interference should be used for all subsequent determinations.

Alternately, a plot of Absorbance vs. milliliters of extract added can be constructed (see Figure A-1). The dilution determined for the point at which the plot becomes linear (99.9% for last three points) is the point where the chemical interference of molecular iodine becomes minimal.

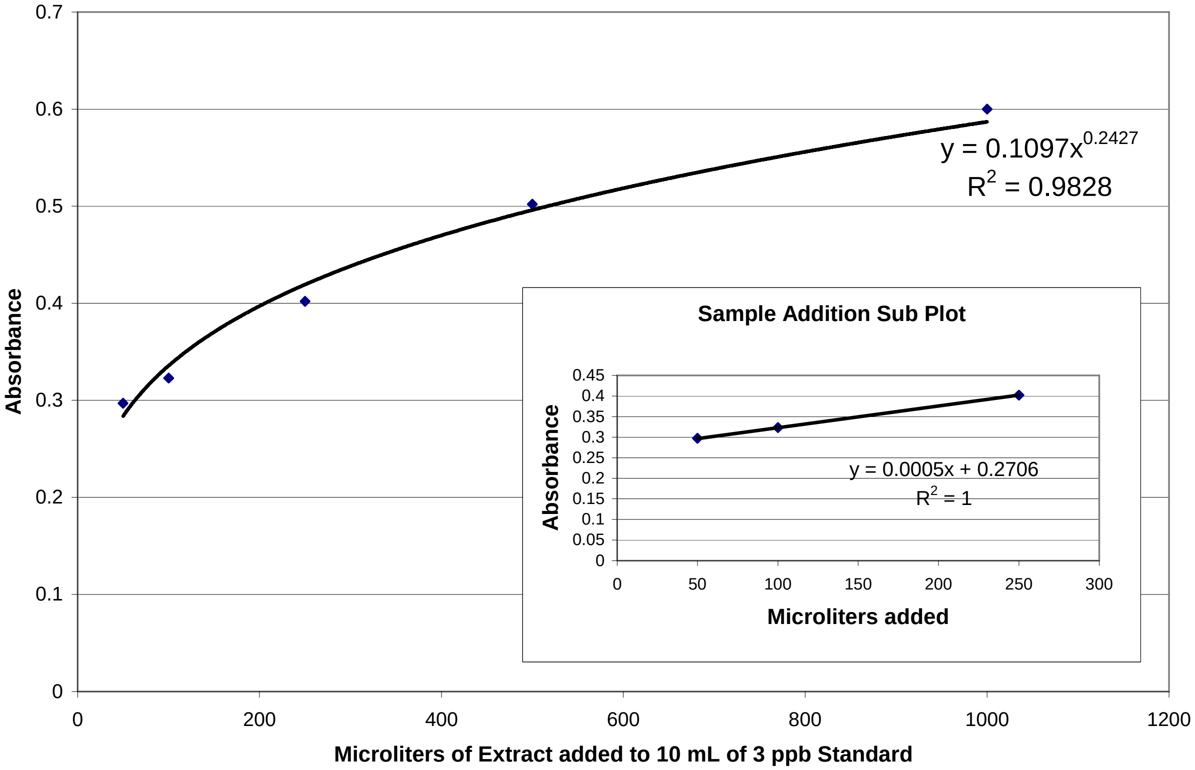

Figure A-5
Example of a Sample Addition Plot

B

PROJECT DATA

B.1 Phase I Data

Data for Phase I Samples
First Batch of Samples

Spike verification laboratory (Draft Method 324)	Low	Medium	High
	276	2139	7941
	249		7713
	258	2466	7531
	244	2430	7349
	240	2284	7395
Average	**253.4**	**2329.75**	**7585.8**

Spike verification laboratory (TD)	Low	Medium	High
	227	2110	7760
	235	2340	7630
	254	2380	7570
	246	2020	7670
	257	2280	7410
Average	**243.8**	**2226**	**7608**

Lab 1 (M6414)	Low	Medium	High
	182	2010	5414
	BDL	3640	46150
	217	850	16950
	130	840	25200
	213	2350	7390
	213	2300	6850
	224	2370	6000
	223	2605	8059
	246	2384	6883
	252	2644	8554
Average	**211**	**2199**	**13745**

B.1 Phase I Data (continued)

Lab 2

(M6414/AFS)	Low	Medium	High
	26	2260	6610
	27	2470	7530
	27	2580	7210
	254	2020	6490
	279	2010	6325
	288	2220	3490
	321	2230	4735
	367	3350	6100
	510	2275	5650
	365	2240	6750
Average	**246**	**2366**	**6089**

Lab 2

(M6414/AAS)	Low	Medium	High
	60	2477	8010
	62	2719	8095
	62	2620	7682
		1926	7454
		1898	7308
		2155	4500
		2131	4577
		2113	5941
		2027	5445
		2153	6094
Average	**61**	**2222**	**6511**

Lab 3

(M6414)	Low	Medium	High
	149	1905	5415
	129	1104	3594
	147	1833	5788
	203	1844	7352
	212	1162	7627
	270	1143	7206
	225	2289	8593
	258	2800	7762
		2604	7248
		2300	7771
Average	**199**	**1898**	**6836**

Lab 4

(M6414)	Low	Medium	High
	8	2828	7485
	114	1545	7750
	203	2215	8375
	203	2467	7882
	92	2490	7615
	210	2590	8205
	197	2550	7438
	209	2510	7450
		2590	7480
			7510
Average	**155**	**2421**	**7719**

Lab 5

(M6414)	Low	Medium	High
	457	4695	
	376	5250	
Average	**417**	**4973**	

Second Batch of Phase I Samples

Spike verification laboratory

(TD)	Low	Medium	High
	259	2530	7880
	235	2600	7730
	247	2510	7660
Average	**247**	**2547**	**7757**

Lab 7

(324)	Low	Medium	High
	247	2476	7218
	239	2666	8258
Average	**243**	**2571**	**7738**

Lab 6

(DC)	Low	Medium	High
	279	3102	7021
	270	3178	8587
	279	2853	7742
	271	2823	9612
	268	2850	6890
	264	3023	9811
	266	2913	8294
	259	3018	8648
	263	2849	7788
	266	3297	8825
Average	**269**	**2991**	**8322**

B.1.1 Phase I Data Selected for ASTM E 691 Calculations

Phase I Data Selected for E 691 Calculation

Spike verification lab (TD)

235	2110	7570
246	2280	7630
254	2340	7670
257	2380	7760

Lab 1 (M6414)

223	2370	6850
224	2384	6883
246	2605	8059
252	2644	8554

Lab 2 (M6414)

288	2240	6100
321	2260	6325
365	2275	6490
367	2470	6610

Lab 3 (M6414)

212	2289	7352
270	2800	7627
225	2604	7762
258	2300	7771

Spike verification lab (324)

240	2284	7395
244	2430	7349
249	2139	7713
258	2466	7531

Lab 4 (M6414)

203	2467	7510
203	2490	7615
209	2510	7750
210	2550	7882

Lab 6 (DC)

261	2491	7593
263	2494	7638
263	2546	8135
265	2638	8422

B.2 Phase II Data

B.2.1 Original Round Robin Data

EPRI Round Robin Raw Data, no Blank Corrections, ng mercury

Actual Spike Level (ng)	TD-1	TD-2	DC	324-1	324-2	324-3	M6414-1	M6414-2	M6414-3	M6414-4	M6414-5
39.9	38	24	26.6	39.7	42.1	24	15	25.3	34	BDL	40
	39	29	26.9	29.9	41	62	20	24.5	33.5	BDL	33
	40	29	30.7	28.6	38.2	64	20	16.7	40.5	BDL	39
	39	32	24.8	31.5	30	19	15	19.9	39.5	BDL	54
	38	33.0	23.4	29.1	38.9	57		14.1	36	BDL	32
248.9	248.5	248	226	199.1	218.9	224	145	138.6	204.5	BDL	246
	240.2	234	235	210.5	216.4	368	125	151.3	200	BDL	249
	252.1	245	244	205.0	226.5	296	130	140.3	217.5	BDL	248
	255.5	242	247	217.7	219.5	283	125	133.7	215.5	BDL	244
	251.1	247.0	240	180.8	217.4	281	135	141.9	183.5	BDL	244
2491	2457.2	2390	2585	2000.2	2160	2868	1205	1518	1680	1800	2452
	2517.1	2250	2587	2200.8	2248	**4483**	1375	1391	1850	1818	2363
	2516	2280	2608	2029.0	2209.1	2935	1245	1435	1928	1808	2458
	2510	2240	2637	2000.2	2245.5	2234	1285	1430	1805	1275	2445
	2458.5	2340	2671	2114.8	2226	**	1245	1386	1868	1377	2447
8967.6	8932	8490	9035	7927.3	8435.8	8279	5190	5775	6320	6350	8732
	8833	8490	9167	7630.1	8552.7	99.09	6175	5500	6720	6758	8686
	9087	8370	9208	7927.3	9624.5	8592	6965	5445	7930	6630	8749
	9071	8100	9242	7877.7	9636.1	9407	7285	5280	6780	6706	8765
	9154.2	8370	9286	7878.0	8207.4	9732	7275	5374	7260	5942	8594

B.2.1 Original Round Robin Data (continued)

Actual Spike Level (ng)	TD-1	TD-2	DC	324-1	324-2	324-3	M6414-1	M6414-2	M6414-3	M6414-4	M6414-5
24910.1	25113	19600	24880	23344.5	23882.9	25486	14635	12250	18800	17978	23634
	25345	19000	25930	23561.4	23558.7	22593	19335	12700	21100	18641	23683
	25400.1	20100	25130	22570.6	24098.6	26931	20135	12000	27250	18870	23770
	24915	21400	25340	23375.5	24057.1	25522	18965	11500	23700	13133	23927
	24232	20900.0	25450	21795.5	22772.1	26451	**215**	11350	**	15734	23901
39856.1	39703.1	34000	39370	37023.1	39833.5	38579	26000	19150	31725	32256	38603
	38309.4	32400	38990	36528.0	41147.6	37093	28900	17750	43875	32319	38423
	38812	31900	38370	35659.9	38367.4	35540	30735	18750	43500	29610	38615
	39137	32600	39230	35226.1	38673	38608	28900	17800	31350	30240	38595
	39558	30700	39230	36217.8	40930.9	37417	25365	18700	1500	32538	38837

** Tube broken and sample lost

Bold identifies suspicious value

324-3	M6414-1	M6414-3	
3130	14657	30390	Average of all in level
4483	**215**	**1500**	**Outliers**
2679	18267.5	37612.5	Average without outlier
386.8	2470.4	7018.1	Std Dev
4.66 s	7.3 s	5.15 s	No. of std dev's difference
			Okay to drop outliers

B.2.1 Phase II Corrected Data

Phase II Data after Correcting for Reagent Blanks and Dropping Outliers

Actual Spike (ng)	TD-1	TD-2	DC	324-1	324-2	324-3	M6414-1	M6414-2	M6414-3	M6414-4	M6414-5
39.9	38	24	26.6	39.7	41.0	16.9	15	25.3	34	BDL	40
	39	29	26.9	29.9	40.2	55.8	20	24.5	33.5	BDL	33
	40	29	30.7	28.6	37.4	58.4	20	16.7	40.5	BDL	39
	39	32	24.8	31.5	29.1	11.9	15	19.9	39.5	BDL	54
	38	33.0	23.4	29.1	38.0	50.9		14.1	36	BDL	32
248.9	248.5	248	226	199.1	218.7	216.9	145	138.6	204.5	BDL	246
	240.2	234	235	210.5	216.1	361.8	125	151.3	200	BDL	249
	252.1	245	244	205.0	226.2	289.7	130	140.3	217.5	BDL	248
	255.5	242	247	217.7	219.2	277.5	125	133.7	215.5	BDL	244
	251.1	247.0	240	180.8	217.2	274.9	135	141.9	183.5	BDL	244
2491	2457.2	2390	2585	2000.2	2159.9	2866.5	1205	1518	1680	1800	2452
	2517.1	2250	2587	2200.8	2248.0		1375	1391	1850	1818	2363
	2516	2280	2608	2029.0	2209.0	2924	1245	1435	1928	1808	2458
	2510	2240	2637	2000.2	2245.4	2233.3	1285	1430	1805	1275	2445
	2458.5	2340	2671	2114.8	2225.9		1245	1386	1868	1377	2447
8967.6	8932	8490	9035	7927.3	8433.6	8278.3	5190	5775	6320	6350	8732
	8833	8490	9167	7630.1	8550.5	9908.9	6175	5500	6720	6758	8686

B.2.1 Phase II Corrected Data (continued)

Actual Spike (ng))	TD-1	TD-2	DC	324-1	324-2	324-3	M6414-1	M6414-2	M6414-3	M6414-4	M6414-5
	9087	8370	9208	7927.3	9622.3	8591.3	6965	5445	7930	6630	8749
	9071	8100	9242	7877.7	9633.9	9406	7285	5280	6780	6706	8765
	9154.2	8370	9286	7878.0	8205.2	9731.8	7275	5374	7260	5942	8594
24910.1	25113	19600	24880	23344.5	23882.9	25485.4	14635	12250	18800	17978	23634
	25345	19000	25930	23561.4	23558.7	22592.9	19335	12700	21100	18641	23683
	25400.1	20100	25130	22570.6	24098.6	26930.9	20135	12000	27250	18870	23770
	24915	21400	25340	23375.5	24057.1	25522.1	18965	11500	23700	13133	23927
	24232	20900.0	25450	21795.5	22772.1	26450.3		11350		15734	23901
39856.1	39703.1	34000	39370	37023.1	39833.5	38578.9	26000	19150	31725	32256	38603
	38309.4	32400	38990	36528.0	41147.6	37091.9	28900	17750	43875	32319	38423
	38812	31900	38370	35659.9	38367.4	35539.9	30735	18750	43500	29610	38615
	39137	32600	39230	35226.1	38673.0	38606.8	28900	17800	31350	30240	38595
	39558	30700	39230	36217.8	40930.9	37416.6	25365	18700		32538	38837

B.2.2 Phase II Round Robin Data Used for Preparing Charts

Spike Level	**TD-1**	**TD-2**	**DC**	**324-1**	**324-2**	**324-3**	**M6414-1**	**M6414-2**	**M6414-3**	**M6414-4**	**M6414-5**
	% Recovery - 6 levels										
Average	99.42	86.53	94.90	85.71	94.05	102.84	60.80	53.31	85.16	70.89	97.54
	% RSD - 6 levels										
Avg % RSD	1.75	4.57	3.14	5.39	4.90	18.05	10.60	7.30	10.65	10.12	4.41
	% Recovery - 5 levels										
Average	99.9	89.1	100.6	86.9	94.2	104.0	64.2	53.9	83.8	70.9	97.2
	% RSD - 5 levels										
Avg % RSD	1.67	3.09	1.69	3.58	3.33	10.07	9.42	3.93	11.0	10.120	0.853
Spike Level	**% RSD 6 levels**		**% RSD 4 Closest Results**								
39.9	18.11		11.88								
248.9	5.36		2.13								
2491	5.24		1.47								
8967.6	4.85		2.75								
24910.1	6.31		1.57								
39856.1	4.49		1.51								
	% Recovery - 2 Closest Levels for QCS										
248.9	100.2	97.7	95.8	81.4	88.2	114.2	53.0	56.7	82.0		98.9
2491	100.0	92.3	105.1	83.1	89.0	107.4	51.0	57.5	73.3	64.9	97.7
Average	100.1	95.0	100.4	82.2	88.6	110.8	52.0	57.1	77.7	64.9	98.3
QCS	100	101	92.1		98.5	94.6	57.9	82.6		78.1	94.7

B.2.2 Phase II Round Robin Data Used for Preparing Charts (continued)

Spike Level	TD(2)	DC(1)	324(3)	M6414(5)
248.9	98.97	95.78	94.58	72.68
2491	96.18	105.08	93.15	68.87
8967.6	96.90	102.45	96.35	76.36
24910.1	90.73	101.75	96.35	75.15
39856.1	89.60	97.95	94.81	77.29

% Recovery - 5 levels

Spike Level	TD (not Blind)	DC	324	M6414
248.9	100.23	95.78	88.18	98.92
2491.0	100.03	105.08	89.03	97.67
8967.6	100.53	102.45	99.12	97.07
24910.1	100.36	101.75	95.04	95.48
39856.1	98.11	97.95	99.84	96.89

Consumer Energy Study Data

Carbon Mass	% Recovery
0.5134	96.61
1.0146	91.72
1.5042	87.78
2.0137	82.84
2.5243	75.93

C
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