METHOD 7474

MERCURY IN SEDIMENT AND TISSUE SAMPLES
BY ATOMIC FLUORESCENCE SPECTROMETRY

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method uses atomic fluorescence spectrometry to determine the following RCRA analyte in sediment and tissue samples:

Analyte	CAS Number*
Mercury, total	7439-97-6

* Chemical Abstracts Service Registry Number

1.2 The range of this method is from approximately 1 part per billion to the part per million range. Analysis of the entire range cannot be accomplished at once, but rather different portions of this range can be analyzed depending upon the instrument gain settings.

1.3 Prior to employing this method, analysts are advised to consult the manufacturer's instructions for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.4 Use of this method is restricted to use by, or under supervision of, properly analysts experienced and trained in the analysis of trace elements at very low concentrations

(ppb range). Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A representative portion of sample is digested in a microwave unit (a variation of Method 3051) using nitric and hydrochloric acids in a closed fluorocarbon container. The sample is digested under pressure to aid in the dissolution of organic compounds containing mercury.

2.2 An aliquot of the digested sample is diluted and subjected to cold digestion with an acid/bromate/bromide mixture.

2.3 Stannous chloride is added to the digested sample as a reducing agent to produce Hg^0. The reduced mercury is separated from the sample/reagent mixture as a vapor that is carried to the fluorescence detector by a stream of high purity argon.

3.0 DEFINITIONS

Refer to Chapter One, Chapter Three, and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method for specific guidance on quality control procedures and to Chapter Three for general guidance on the cleaning of glassware. Also refer to Method 7000 for a discussion of interferences.

4.2 Method 3052 may overcome the problems associated with incomplete digestion of complex matrices. Incomplete digestion may lead to the incomplete solubilization of sparingly soluble Hg compounds. The reader is encouraged to review the guidance provided in Method 3052 for the appropriate acid and reagent combinations.

4.3 High purity argon (99.999%) must be used as the carrier gas. Nitrogen will reduce the sensitivity by a factor eight-fold, while the use of air will reduce the sensitivity thirty-fold.

4.4 The presence of water vapor in the fluorescence detector may produce scattering effects, positive interferences and degradation of the analytical signal. The use of a dryer tube is necessary to remove any water vapor from the flow before reaching the detector.

4.5 Contamination is always a potential problem in trace element determinations. See Chapter Three for guidance regarding clean laboratory procedures.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 Many mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care must be exercised in the handling of concentrated mercury reagents. Concentrated mercury reagents should only be handled by analysts knowledgeable of their risks and of safe handling procedures.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application is demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 Atomic fluorescence system:

6.1.1 Autosampler (optional) -- A multi-position computer controlled autosampler may be used. However, it is essential that the autosampler have a wash cycle or "wash pot" to rinse the probe between sampling positions. The autosampler wash water should closely approximate the wash water (Sec. 7.13) in acid strength.

6.1.2 Peristaltic pump -- A three-channel peristaltic pump that must be able to deliver reagents and sample at flow rates up to 10 mL/min by varying the pump speed, the pump tubing, or both. Silicone pump tubing is required for analyte determinations in the part-per-trillion (ppt) range because PVC pump tubing has been found to adsorb mercury.

6.1.3 Solenoid switching valve -- A software-controlled valve is required to switch between wash and sample at the proper intervals in the analysis cycle.

6.1.4 Mass flow controllers -- Mass flow controllers are required for the carrier and sheath gas flows when analyzing near the quantitation limit where maximum stability of conditions are critical.

6.1.5 Gas liquid separator -- A gas-liquid separator is required to sparge reduced mercury from the liquid stream, direct the mercury vapor and argon carrier gas to the fluorescence detector, and direct the liquid reagents to waste.

6.1.6 Dryer tube -- A dryer tube is to be placed in line between the gas-liquid separator and the detector to remove water vapor from the carrier gas stream. Any dryer tube which does not degrade the analysis or sensitivity is acceptable. (PermaPure MD-250-12 or equivalent.)

6.1.7 Fluorescence detector -- A fluorescence detector with a high intensity mercury light source and a photomultiplier tube at a right angle to the source is required. Use of 254 nm filter coupled with the chemistry of the stannous chloride reduction in the vapor generator/gas-liquid separator makes the detector highly specific for mercury.

6.1.8 Computer controller -- A computer controller and software is required to operate and coordinate the various components of the system and acquire the data as it is produced.

6.1.9 Argon gas supply -- High purity argon (99.999%) is required. A gas purifier cartridge is also recommended.

6.1.10 Microwave apparatus -- Refer to Method 3051 for a description of an appropriate microwave digestion apparatus.

6.2 Data systems recorder -- A recorder is recommended so that there will be a permanent record and any problems with the analysis can be easily recognized.

6.3 Pipets -- Microliter, with disposable tips. Pipet tips should be checked as a possible source of mercury contamination prior to their use. Class A pipets can be used for the measurement of volumes equal to or larger than 1 mL.

6.4 Glassware -- All glassware, vessels, pipets, etc., must be very clean. Glass, plastic, and fluorocarbon polymer (PFA or TFM) containers may be used but polymers are not suitable for samples containing metallic mercury. The following is an example of a cleaning procedure successfully used in a trace level laboratory: Soak glassware overnight in a cleaning solution (such as Micro®). Rinse four times with Type I water (ASTM Type I water) and soak overnight in an acid/bromate/bromide mixture. The acid/bromate/bromide mixture is made by adding the bromate/bromide solution from Sec. 7.9 to dilute acid (approximately 5% v/v) until a yellow color forms (the exact composition is not critical). The container should be covered or closed, as an open container will pick up mercury from the atmosphere and permit bromine vapor to escape to the air. After soaking overnight, add enough 5% hydroxylamine from Sec. 7.10 to eliminate the yellow color. Rinse six times with Type I water. Cap the glassware tightly if it is not to be used immediately. Store in a reduced mercury atmosphere.

When running samples on a daily basis, the rigorous cleaning procedure described above should be applied every 5 to 7 uses. In between and after each use, soak the vessels in cleaning solution for 2 hr to loosen deposits. Clean the vessels thoroughly with cotton swabs (tested for mercury contamination) and soaked them again in cleaning solution overnight. Rinse six times with reagent water. Repeat the soaking and rinsing steps if necessary.

6.5 Balance -- Top-loader balance with an accuracy of $\pm$ 0.01 g.

6.6 Muffle furnace -- A muffle furnace capable of reaching and maintaining a temperature of 150 ^{o}C is required for purifying the potassium bromate and potassium bromide reagents.

7.0 REAGENTS AND STANDARDS

7.1 Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other

grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Reagent water -- Reagent water should be interference free. All references to water in this method refer to reagent water unless otherwise specified.

7.3 Nitric acid, HNO_3 -- Use a trace metal grade with negligible mercury content. If the reagent blank is less than the lowest limit of detection, the acid may be used.

7.4 Hydrochloric acid, HCl -- Use a trace metal grade with negligible mercury content. If the reagent blank is less than the lowest limit of detection, the acid may be used.

7.6 Mercury stock standard solution -- Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL (1.0 mL = 1.0 mg Hg). Alternatively, a mercury stock solution may be purchased from a reputable source with a concentration of 1.0 mg Hg/mL. Verify the quality of the standard by checking it against a second source standard (see second paragraph of Sec. 9.4).

7.7 Potassium bromate (CAS Number 7758-01-2) -- Volatilize trace mercury impurities by heating in a muffle furnace at 150 °C for at least 8 hr. This procedure is recommended every time the compound is used. However, the reagent may be stored in a desiccator between uses if it can be demonstrated that is not contaminated prior to use. This may be accomplished by performing a reagent blank analysis of the bromate/bromide solution (Sec. 7.9).

7.8 Potassium bromide (CAS Number 7758-02-3) -- Volatilize trace mercury impurities by heating in a muffle furnace at 150 °C for at least 8 hr. This procedure is recommended every time the compound is used. However, the reagent may be stored in a desiccator between uses if it can be demonstrated that is not contaminated prior to use. This may be accomplished by performing a reagent blank analysis of the bromate/bromide solution (Sec. 7.9).

7.9 Bromate/bromide solution -- Dissolve 1.39 g potassium bromate and 5.95 g potassium bromide in 500 mL reagent water. Prepare weekly.

7.10 Hydroxylamine hydrochloride (CAS Number 5470-11-1) -- Use a source that is specified as suitable for mercury analysis.

7.11 Hydroxylamine hydrochloride solution (5% w/v) -- Dissolve 2.5 g hydroxylamine in 50 mL of reagent water. Prepare weekly.

7.12 Stannous chloride solution, 2% in 10% HCl -- Add approximately 500 mL of reagent water to a 1 L volumetric flask followed by the addition of 100 mL conc. HCl. Add 20.0 g stannous chloride and stir to dissolve. Dilute to 1 L with reagent water. The solution should be sparged with argon for 30 min prior to analysis to remove any traces of mercury. Prepare daily.

7.13 Wash water (reagent blank), 5% HCl -- Add approximately 1000 mL of reagent water to a 2 L flask. Add 100 mL conc. HCl and 80 mL of the bromate/bromide solution (Sec. 7.9). Bring to volume with reagent water. Prepare daily.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Three, "Inorganic Analytes."

8.2 All sample containers must be prewashed with detergents, acids, and reagent water. Glass, plastic, and polytetraflouroethylene (PTFE) containers are suitable in most cases. Polymers are not suitable for samples containing metallic mercury.

8.3 Metallic mercury, some inorganic mercury compounds, and many organic mercury compounds are volatile and unstable. It is advantageous to analyze the samples as soon as possible to determine the total mercury in the sample but in no case exceed the 28-day limit as defined in Chapter Three of this manual. Non-aqueous samples must be analyzed as soon as possible. If solid samples are not analyzed immediately, refrigeration is necessary.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for additional guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency by following the sample preparation and analytical procedures described in this method and generating data of acceptable accuracy and precision for the target analyte (mercury) in a clean matrix. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made.

9.3 For each batch of samples processed, at least one method blank must be carried throughout the entire sample preparation and analytical process. A method blank is prepared by using a volume or weight of reagent water at the volume or weight specified in the preparation method and then carried through the appropriate steps of the analytical process. These steps may include but are not limited to digestion, dilution, filtering, and analysis. If the method blank does not contain the target analyte at a level that interferes with the project-specific data quality objectives then the method blank would be considered acceptable. In the absence of project-specific data quality objectives, if the blank is less than the lower level of quantitation or less than 10% of the lowest sample concentration for the analyte, whichever is greater, then the method blank would be considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once and if still unacceptable then all samples after the last acceptable method blank must be reprepped and reanalyzed along with the other appropriate batch QC samples. These blanks will be useful in determining if samples are being contaminated.

9.4 For each batch of samples processed, at least one laboratory control sample must be carried throughout the entire sample preparation and analytical process. The laboratory control samples should be spiked with each analyte of interest at the project-specific action level or, when lacking project-specific action levels, between the low and midlevel standards. Acceptance criteria should be set at a laboratory derived limit developed through the use of historical analyses. In the absence of historical data this limit should be set at ± 20% of the

spiked value. After the determination of historical data, ± 20% should still be the limit of maximum deviation to express acceptability. If the laboratory control sample cannot be considered acceptable, the laboratory control sample should be re-run once and if still unacceptable then all samples after the last acceptable laboratory control sample must be reprepped and reanalyzed. Refer to Chapter One for more information.

If more than 10 samples per day are analyzed, the working standard curve must be verified by measuring satisfactorily a LCS or mid-range standard or reference standard after every 10 samples. This sample value should be within 20% of the true value, or the previous 10 samples must be reanalyzed.

9.5 Matrix spike/matrix spike duplicates (MS/MSDs) -- MS/MSDs are intralaboratory split samples spiked with identical concentrations of each analyte of interest. The spiking occurs prior to sample preparation and analysis. An MS/MSD is used to document the bias and precision of a method in a given sample matrix. Based on the analyst's discretion, a separate spike sample and a separate duplicate sample may be analyzed in lieu of the MS/MSD. For each batch of sample processed, at least one MS/MSD sample must be carried throughout the entire sample preparation and analytical process. MS/MSD samples should be spiked at the same level as the corresponding laboratory control sample that is at the project-specific action level or, when lacking project-specific action levels, between the low and midlevel standards. Acceptance criteria should be set at a laboratory derived limit developed through the use of historical analyses. In the absence of historical data this limit should be set at ± 20% of the spiked value for precision and # 20 relative percent difference (RPD). After the determination of historical data, 20% should still be the limit of maximum deviation for both percent recovery and relative percent difference to express acceptability.

9.6 The method of standard additions can be used to verify linearity or if matrix interference is suspected. Refer to Method 7000 for standard addition procedures.

9.7 Refer to Method 7000 for additional QA and QC information that may be applicable.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Calibration standards -- All analyses require that a calibration curve be prepared to cover the appropriate concentration range. Calibration standards are prepared by diluting the stock metal solutions at the time of analysis and digesting them using the same procedure used for actual samples. If running more than one batch of samples during the same week, the microwave-digested standards can be kept in clean dedicated glassware from which dilutions can be made daily which are then prepared with acid and bromate/bromine just as the samples are prepared after microwaving.

10.1.1 Calibration standards must be prepared fresh (or from the weekly microwave digest described in Sec. 10.1) each time a batch of samples is analyzed. Prepare a reagent blank and at least three calibration standards in graduated amounts in the appropriate range of the linear part of the curve.

10.1.2 The calibration standards should be prepared using the same type of bromine, acid or combination of acids and at the same concentration as will result in the samples following processing.

10.2 A calibration curve must be prepared each day with a minimum of a reagent blank and three standards. After calibration, the calibration curve must be verified by use of an initial

calibration blank (ICB) and an initial calibration verification (ICV) standard. The ICV standard is made from a reference material or other independent standard material at or near the mid-range. The ICV recovery must be within +/- 10% of its true value and the ICB must be less than the lowest limit of quantitation for the curve to be considered valid. If the calibration curve cannot be verified, the cause must be determined and the instrument recalibrated before sample analysis.

10.3 The calibration curve must also be verified at the end of each analysis batch and/or after every ten samples by measuring satisfactorily a mid-range standard or check standard (continuing calibration verification (CCV) standard) and a reagent blank (continuing calibration blank or CCB). The CCV must be measured within 10% of its true value and the CCB must be less than the lower limit of quantitation for the curve to be considered valid. If the aforementioned criteria are not met, reanalyze the samples analyzed since the last passing CCV and calibration blank.

11.0 PROCEDURE

11.1 Prepare samples in a microwave unit using only nitric and hydrochloric acids. The digestion procedure described below (Secs. 11.1.1 and 11.1.2) is a modification of Method 3051, refer to Method 3051 for more details on setting up and operating the microwave digestion system. Also, due to the rapid advances in microwave technology, consult your manufacturer's recommended instructions for guidance on their microwave digestion system and refer to this manual's "Disclaimer" when conducting analyses using this method.

11.1.1 Transfer approximately 1.0 g of wet sample to a digestion vessel. Add 2.0 mL of concentrated nitric and 6.0 mL of concentrated hydrochloric and cap.

11.1.2 Microwave the samples with a program appropriate for complete digestion. Typically, the temperature should be ramped slowly to 190 EC without overpressurization and held at 190 EC for 10 min or until the digestion is complete.

11.1.3 Cool the samples. During the cooling period, vent and swirl the samples occasionally to release dissolved gases. After the samples have cooled and the dissolved gases have been dissipated, transfer 1.0 mL of the digested sample into a graduated 50 mL centrifuge tube that contains reagent water, 2.0 mL bromate/bromide solution (Sec. 7.9) and 2.5 mL HCl. Bring to volume with reagent water and allow to digest at room temperature for 15 min. Document the accuracy of the centrifuge tubes through mass/volume records or use volumetric glassware.

11.2 Set up a software-controlled timing sequence for the analysis. Follow your instrument manufacturer's instructions for all settings. Timing sequences that should be addressed are:

11.2.1 Delay -- The delay step allows times for the sample line to fill with sample.

11.2.2 Rise -- The rise step allows sample to enter the gas/liquid separator and react with the stannous chloride. Mercury in the digested sample is reduced to Hg^0 and the argon carrier stream carries the Hg^0 as mercury vapor to the detector.

11.2.3 Analysis -- The analysis time allows for the peak height to rise to its maximum while the software measures the peak height or area.

11.2.4 Memory -- The memory time allows the signal to return to the baseline level.

11.2.5 Set the gas flows at a level providing adequate sensitivity for the desired analytical range. Flow rates for the carrier gas, sheath gas, and dryer tube gas should be established.

11.2.6 When using a variable speed peristaltic pump, choose appropriate sized tubing to obtain an approximate ratio of 2:1 between sample/wash (Sec. 7.13) flow rates and the reductant (Sec. 7.12) flow rate.

11.2.7 Set the gain on the detector to the sensitivity range required for the analysis.

11.2.8 If an autosampler is used, set up a wash solution for the autosampler probes. The autosampler wash solution should closely approximate the wash water (Sec. 7.13) in acid concentration or contain acid at a sufficient strength (typically 5%) to preclude any sample carryover.

11.2.9 Allow 30 min for the system to equilibrate before initiating sample analysis.

11.3 Sample analysis

11.3.1 Add 0.10 mL of the hydroxylamine solution (Sec. 7.11) to each sample and standard to remove excess bromine and decolorize the sample.

11.3.2 Allow precipitate or sediment in diluted samples to settle to avoid fouling the valves with solid material during analysis.

11.3.3 Any sample that gives a response greater than the highest standard must be diluted and rerun. Add appropriate amounts of reagents to ensure the reagent concentration of the diluted sample match that of the other samples and the wash (Sec. 7.13).

11.3.4 Any samples that fall outside the laboratory calculated and derived QC range must be re-digested and reanalyzed.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Maintain an instrument log book that contains all information necessary to reproduce the analytical conditions associated with a sample run.

12.2 Sample calculation --

$$\mu g/kg \text{ of } Hg = \frac{\text{detected ng Hg}}{\text{L}} \times \frac{\text{0.008 L of dig. solution}}{\text{grams of sample}} \times \frac{\text{final volume of 0.05 L}}{\text{0.001 L digested sample}}$$

When moisture corrected reporting is required, the concentration results for all sample matrices calculated as noted in this section may be converted to moisture corrected results as follows:

$$\text{Moisture corrected concentration} = \frac{(\text{As received concentration})}{(100 - \%\ \text{Moisture})} \times 100$$

where the percent moisture is determined by drying an aliquot of the sample at 105 EC overnight. The % moisture is calculated as follows:

$$\%\ \text{moisture} = \frac{\text{g of sample} - \text{g of dry sample}}{\text{g of sample}} \times 100$$

12.3 Results need to be reported in units commensurate with their intended use and all dilutions need to be taken into account when computing final results.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance goals for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 Accuracy -- Results for accuracy from the US EPA Region IV laboratory are given in Table 1. Data for liquid reference materials and liquid calibration checks used with this procedure are included along with the sediment and tissue materials. These data are provided for guidance purposes only.

13.3 Precision -- Results for precision from the Region IV laboratory are provided in Table 2. These data are provided for guidance purposes only.

13.4 The U.S. EPA's Region IV laboratory also participated in three intercomparison studies, which are described below.

13.4.1 In the first study, two sediments and two tissues were analyzed for the National Oceanic and Atmospheric Administration in the "Seventh Round Intercomparison for Trace Metals in Marine Sediments and Biological Tissues."

13.4.1.1 The accepted value for the sample identified as Sediment T was 0.107 mg/kg with an acceptable range of 0.087 to 0.127. The value reported from this laboratory was 0.100 with a standard deviation of 0.003 and percent relative standard deviation of 3.0. Thirty-two laboratories reported results for this sample. These data are provided for guidance purposes only.

13.4.1.2 The accepted value for the sample identified as BCSS-1 was 0.163 mg/kg with an acceptable range of 0.096 to 0.230. The value reported from this laboratory was 0.199 with a standard deviation of 0.013 and percent relative standard deviation of.3. Twenty-eight laboratories reported results for this sample. These data are provided for guidance purposes only.

13.4.1.3 The accepted value for the tissue sample identified as Tissue S was 0.0618 mg/kg with an acceptable range of 0.0409 to 0.0827. The value reported from this laboratory was 0.0574 with a standard deviation of 0.0047 and percent relative standard deviation of 8.3. Thirty-three laboratories reported results for this sample. These data are provided for guidance purposes only.

13.4.1.4 The certified value for the tissue sample identified as NIST 1566a was 0.0642 mg/kg with an acceptable range of 0.0575 to 0.0709. The value reported from this laboratory was 0.0631 with a standard deviation of 0.0042 and percent relative standard deviation of 6.8. Twenty-seven laboratories reported results for this sample. These data are provided for guidance purposes only.

13.4.2 Two sediments and two tissues were analyzed in the "Eighth Round Intercomparision for Trace Metals in Marine Sediments and Biological Tissues for the National Oceanic and Atmospheric Administration."

13.4.2.1 The accepted value for the sediment sample identified as Sediment U was 0.55 mg/kg with an acceptable range of 0.42 to 0.68. The value reported from this laboratory was 0.63 with a standard deviation of 2.7. The number of laboratories reporting results for this sample was 28. These data are provided for guidance purposes only.

13.4.2.2 The accepted value for the sediment sample identified as BCSS-1 was 0.180 mg/kg with an acceptable range of 0.109 to 0.251. The value reported from this laboratory was 0.23 with a standard deviation of 0.01 and percent relative standard deviation of 5.7. The number of laboratories reporting results for this sample was 26. These data are provided for guidance purposes only.

13.4.2.3 The accepted value for the tissue sample identified as Tissue V was 0.0654 mg/kg with an acceptable range of 0.0462 to 0.0846. The value reported from this laboratory was 0.058 with a standard deviation of 0.006 and percent relative standard deviation of 8.0. The number of laboratories reporting results for this sample was 32. These data are provided for guidance purposes only.

13.4.2.4 The certified value for the tissue sample identified as NIST 1566a was 0.0654 mg/kg with an acceptable range of 0.0587 to 0.0721. The value reported from this laboratory was 0.066 with a standard deviation of 0.003 and percent relative standard deviation of 5.2. The number of laboratories reporting results for this sample was 28. These data are provided for guidance purposes only.

13.4.3 Ten sediment samples from the Florida Everglades were analyzed and the results from two laboratories are presented in Table 3. These data are provided for guidance purposes only.

13.5 Comparison data for this method (CVAF) versus cold vapor atomic absorption generated within the Region IV laboratory are presented in Tables 4 and 5. The lowest results in Table 5 are near the limits of detection for the CVAA method, but well within the CVAF range, while the higher results are obtained by diluting samples for the CVAF method, but are well within the range for the CVAA method. Therefore, the CVAA method may be more appropriate for the samples with higher levels of mercury and the CVAF method may be more appropriate for lower level samples. These data are provided for guidance purposes only.

13.6 The following documents may provide additional guidance and insight on this method and technique:

13.6.1 W. Van Delft and G. Vos, *Analytica Chimica Acta*, 209 (1988) 147-156.

13.6.2 "Yorkshire Water Methods of Analysis," 5th Edition, 1988. (ISBN 090507236)

13.6.3 "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

13.6.4 "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, revised January 1976.

13.6.5 "Proposed OSHA Safety and Health Standards, Laboratories," Occupational Safety and Health Administration, FR, July 24, 1986.

13.6.6 Standard Methods, 18th Edition, 1992.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The 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 their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. P. S. Analytical Ltd., "Method for Total Mercury in Drinking Water, Surface, Ground, Industrial and Domestic Waste Waters and Saline Waters," Sevenoaks, Kent, U. K.

2. U. S. EPA, Office of Water, "Method 245.7: Mercury in Water by Cold Vapor Atomic Fluorescense Spectrometry, Draft," EPA-821-D-03-001, December 2003

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the tables referenced by this method. A flow diagram of the procedure follows the tables.

TABLE 1

EXAMPLE RECOVERY DATA FOR SEDIMENT AND TISSUE REFERENCE MATERIALS, SPIKES, METHODS CHECKS (MC), AND CALIBRATION CHECKS

Matrix	True Value[1]	Avg. % Rec.	No. of Samples	Std dev
NIST 8406 SED	60 µg/kg	103.3	70	9.3
NRCC BEST1 SED	92.0 µg/kg	100.9	21	7.4
Sediment spike	22.7 to 68.9 µg/kg	89.2	38	13.7
NIST 1575 Plant tissue	150 µg/kg	95.6	13	7.5
NIST 1566 Oyster tissue	84.2 µg/kg	96.7	72	12.3
NRCC DORM-1 Fish tissue	798 µg/kg	108	9	8.1
NBS 1641B Inorg water (MC)	38 to 60.8 ng/L	95.6	15	6.4
NBS 1641C Inorg water (MC)	36.8 to 73.5 ng/L	105.6	6	4.3
EPA WS024 Inorg+org water	43.2 to 108 ng/L	88.2	16	7.0
EPA WS029 Inorg+org water	10.1 to 50.6 ng/L	97.3	45	7.3
EPA WS030 Inorg+org water	43.2 ng/L	100.6	24	8.6
EPA WS031 inorg+org water	9.08 to 45.4 ng/L	100.8	49	11.1
Calib checks water	20.0 to 100 ng/L	101.5	139	4.2

[1]True values analyzed at various dilutions.

Data taken from Ref. 2.

TABLE 2

EXAMPLE PRECISION DATA FOR SEDIMENT AND TISSUE SAMPLES[1]

Replicates	Avg %RSD	No. of samples	Std dev
Sediment original	10.2	280	9.2
Sediment duplicate	8.8	43	8.8
Sediment original vs duplicate	7.5	43	7.0
Tissue original	11.4	61	10.5
Tissue duplicate	12.0	13	10.6
Tissue original vs duplicate	5.7	13	4.7

[1]All samples analyzed twice.

Data taken from Ref. 2.

TABLE 3

EVERGLADES SEDIMENT SAMPLE COMPARISON DATA (µg/kg)

Sample	Reference Laboratory			Region IV Laboratory	
	Rep 1	Rep 2	Fluorescence Rep 1	Fluorescence Rep 2	Method 245.5
1	11	13	8.6	10.3	--
2	6	--	5.6	5.4	< 25
3	76	--	76	73	68
4	58	--	63	64	59
5	410	--	458	444	424
6	296	--	501	463	453
7	42	--	48	46	--
8	40	--	47	58	--
9	36	--	37	37	--
10	34	40	42	39	--

Data taken from Ref. 2.

TABLE 4

COMPARISON OF CVAF METHOD VS. CVAA METHOD 245.5 RESULTS
ON EVERGLADES SEDIMENTS, PEAT AND MARL (µg/kg)

SAMPLE	AVG	%RSD	CVAA	CVAA %RSD
1	169	2.35	148	11.8
2	197	0.35	248	20.3
3	89	8.04	46	56.6
4	64	6.21	48	26.0
5	28	3.09	23	16.4
6	56	3.76	47	15.4
7	97	2.88	75	22.6
8	172	0.11	161	5.7
9	79	7.89	71	10.0
10	75	4.52	68	8.3
11	79	0.70	76	2.8
12	99	1.54	81	18.1
13	67	1.97	58	12.8
14	146	19.25	130	10.6
15	63	0.52	59	6.3
16	157	0.10	140	10.7
17	144	2.37	144	0.2
18	450	2.55	424	5.5
19	482	6.99	453	5.6
20	247	2.89	226	7.7
21	161	1.97	195	17.8
22	108	4.76	118	7.6
23	278	15.96	356	22.0
24	278	13.71	175	40.0
25	273	2.68	209	23.5
26	456	7.79	285	41.1
27	136	6.83	128	5.42
28	263	3.95	215	17.9
29	89	0.75	80	9.3
30	108	4.79	119	8.4

Data taken from Ref. 2.

TABLE 5

COMPARISON OF CVAF METHOD VS. CVAA METHOD 245.5 RESULTS
ON TISSUE SAMPLES (µg/kg)

Sample	Avg	% RSD	CVAA	%RSD CVAA
Alligator Liver 1	802	18.7	950	15.0
Alligator Liver 2	133	19.9	170	21.1
Alligator Liver 3	216	5.2	230	5.5
Alligator Liver 4	62.7	4.6	72	11.7
Gambusia 1	38.2	6.4	66	47.4
Gambusia 2	165	26.7	120	28.2
Mixed Fish Comp.	70.1	10.6	74	3.4
Bass Filet 1	460	22.2	370	19.4
Bass Filet 2	987	5.5	910	7.2
Bass Filet 3	559	15.9	560	0.2
Bass Filet 4	274	52.8	202	26.9
Bass Filet 5	172	2.6	155	9.5
Catfish Filet 1	62.2	12.3	80	22.3
Catfish Filet 2	133	0.5	150	10.4
Catfish Filet 3	119	7.1	130	7.9
Bluegill Filet 1	36.4	5.1	37	1.6
Bluegill Filet 2	53.7	0.0	36	35.1
Clam Tissue 1	28.5	87.1	25	11.8
Clam Tissue 2	21.1	11.6	30	31.0
Clam Tissue 3	17.6	12.2	30	46.3

Data taken from Ref. 2.

MERCURY IN SEDIMENT AND TISSUE SAMPLES BY ATOMIC FLUORESCENCE SPECTROMETRY