

**Compendium of Methods
for the Determination of
Inorganic Compounds
in Ambient Air**

Chapter IO-5

**SAMPLING AND ANALYSIS
FOR ATMOSPHERIC MERCURY**

Center for Environmental Research Information
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

June 1999

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for the Determination of
Inorganic Compounds
in Ambient Air**

Compendium Method IO-5

**SAMPLING AND ANALYSIS
FOR VAPOR AND PARTICLE
PHASE MERCURY IN AMBIENT AIR
UTILIZING COLD VAPOR ATOMIC
FLUORESCENCE SPECTROMETRY
(CVAFS)**

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Method IO-5

Acknowledgments

This Method is part of the *Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air* (EPA/625/R-96/010a), which was prepared under Contract No. 68-C3-0315, WA No. 2-10, by Midwest Research Institute (MRI), as a subcontractor to Eastern Research Group, Inc. (ERG), and under the sponsorship of the U.S. Environmental Protection Agency (EPA). Justice A. Manning, John O. Burckle, Scott Hedges, Center for Environmental Research Information (CERI), and Frank F. McElroy, National Exposure Research Laboratory (NERL), all in the EPA's Office of Research and Development, were responsible for overseeing the preparation of this method. Other support was provided by the following members of the Compendia Workgroup:

- James L. Cheney, U.S. Army Corps of Engineers, Omaha, NE
- Michael F. Davis, U.S. EPA, Region 7, KC, KS
- Joseph B. Elkins Jr., U.S. EPA, OAQPS, RTP, NC
- Robert G. Lewis, U.S. EPA, NERL, RTP, NC
- Justice A. Manning, U.S. EPA, ORD, Cincinnati, OH
- William A. McClenny, U.S. EPA, NERL, RTP, NC
- Frank F. McElroy, U.S. EPA, NERL, RTP, NC
- William T. "Jerry" Winberry, Jr., EnviroTech Solutions, Cary, NC

This Method is the result of the efforts of many individuals. Gratitude goes to each person involved in the preparation and review of this methodology.

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DISCLAIMER

This Compendium has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Method IO-5
Sampling and Analysis for Vapor and Particle Phase Mercury in
Ambient Air Utilizing Cold Vapor Atomic Fluorescence
Spectrometry (CVAFS)

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Chapter IO-5
SAMPLING AND ANALYSIS FOR ATMOSPHERIC MERCURY

Method IO-5
SAMPLING AND ANALYSIS FOR VAPOR AND PARTICLE PHASE MERCURY IN
AMBIENT AIR UTILIZING COLD VAPOR ATOMIC FLUORESCENCE
SPECTROMETRY

1. Scope

1.1 Elemental mercury (Hg) and most of its derivatives are metabolic poisons which bioaccumulate in aquatic food chains, ultimately reaching concentrations capable of causing neurological and reproductive damage in terrestrial, as well as, aquatic organisms. Atmospheric Hg, although present only in trace amounts, has been established as a significant source of Hg to aquatic environments.

1.2 The widespread use of Hg stems largely from its electrical conductivity, high specific gravity, and fungicidal properties. The major sources of atmospheric Hg include combustion processes (incineration of medical waste, municipal waste, sewage sludge, and hazardous waste, as well as burning of fossil fuels), and manufacturing processes (iron and steel production, mining/smelting operations, cement production, and coke production).

1.3 Mercury compounds in the atmosphere exist in vapor and particulate forms, preferentially partitioning into the vapor phase. Mercury species fall within two main categories: inorganic Hg compounds and organic Hg compounds. The most common form of inorganic Hg is elemental Hg vapor. Other inorganic Hg forms include mercuric chloride (HgCl₂) and mercurous chloride (HgCl). The organic compounds include those compounds in which Hg is covalently bonded to a carbon atom, as in the case of methyl and dimethyl Hg.

1.4 Increased focus on atmospheric Hg pollution has resulted from the Clean Air Act Amendments of 1990. Mercury and its compounds are included in the Title III list of hazardous air pollutants and are subject to standards established under Section 112, including maximum achievable control technology (MACT). Also, Section 112(c)(6) of the 1990 Amendments mandates that Hg (among others) be subject to standards that allow for the maximum degree of emission reduction. These standards are to be promulgated no later than 10 years following the date of enactment. Additionally, within 5 years of the date of enactment, a list of source categories that account for no less than 90 percent of Hg emissions must be established.

1.5 As a result of the congressional mandates, the U.S. Environmental Protection Agency (EPA), state, and local air pollution control agencies are under increased pressure to monitor the trace levels of mercury in the ambient air. In addition, attempts to identify source/receptor relationships for these substances and to develop control programs to regulate emissions have been initiated.

1.6 Previous methods used to collect vapor-phase Hg have relied on the rapid amalgamation between Hg and gold or silver and in some cases the adsorption of Hg onto activated charcoal. Mercury was then quantified using atomic absorption spectrometry or instrumental neutron activation analysis. These methods generally required long-duration samples due to higher detection limits. Collection of vapor-phase Hg was improved with the use of thin gold plating on sand packed in a trap to maximize the surface area for collection (Fitzgerald and Gill, 1979). Improvements to analytical detection limits were also made by employing cold-vapor atomic fluorescence spectrometry (Bloom and Fitzgerald, 1988).

1.7 Previous methods used to collect particulate Hg included trapping particles on quartz wool, which was susceptible to artifact formation due to the adsorption of vapor-phase Hg. Quartz-wool plugs should not be utilized for ambient particulate Hg sampling. Additional methods have included air filtration through quartz fiber filters followed by acid extraction (see Inorganic Compendium Methods IO-2 and IO-3). The acid extraction techniques have, until recently, been plagued by high Hg concentrations in the acid extraction solutions. Acid extraction can be utilized as a suitable alternative to the microwave digestion technique in many applications where precision requirements and detection limits are not limiting factors. Instrumental neutron activation analysis has also been used to quantify mercury in particulates collected on Teflon® filters (Lamborg et al., 1994). Microwave digestion (see Inorganic Compendium Method IO-3.1) has been demonstrated to give equivalent results to acid extraction.

1.8 This method describes procedures for collection and analysis of vapor phase and particulate Hg, in order to provide an EPA-approved, accessible sampling and analytical methodology, for uniform monitoring of atmospheric mercury levels. These procedures have been used successfully in long-term regional monitoring programs, as well as short-term intensive studies. For best results, it is suggested that Method IO-5 be used over Methods IO-2 or IO-3 for sampling and analysis of particulate-phase Hg.

2. Applicable Documents

2.1 ASTM Documents

- D1356 *Definition of Terms Related to Atmospheric Sampling and Analysis*
- D1357 *Practice for Planning the Sampling of the Ambient Atmosphere*

2.2 Other Documents

- U. S. Environmental Protection Agency, *Quality Assurance Handbook for Air Pollution Measurement Systems*, EPA-600/9-76-005.
- U. S. Environmental Protection Agency, *Quality Assurance Handbook for Air Pollution Measurement Systems*, EPA-600/4-77-027a.
- Scientific Publications of Ambient Air Studies (1-12).

3. Method Summary

[Note: This method for collection and analysis of mercury in ambient air takes advantage of the amalgamating property of mercury to a gold surface. In the following description reference is made to gold-coated glass beads only. However, other media have been shown to give equivalent results. These include, but are not limited to, gold-coated sand and a solid gold matrix.]

3.1 The collection of mercury, from ambient air in the vapor and particulate phase, involves use of gold-coated bead traps and glass-fiber filters. The amalgamation process for vapor-phase mercury requires a flow rate low enough to allow adsorption of the mercury in the air to the gold surface. The significantly lower levels of particle-phase mercury on the other hand require a much higher flow rate in order to collect sufficient particle mass for mercury determination. Therefore, separate sampling systems are needed for the collection of mercury in the vapor and particle phases. Accurate flow determinations through both sampling systems are critical in providing accurate Hg concentrations in air.

3.2 Vapor-phase Hg is collected using gold-coated glass bead traps. A Teflon® filter pack with a glass fiber filter is placed in front of the traps to remove particulate material from the air being sampled. Air is pulled through the vapor-phase sampling system using a mass-flow controlled vacuum pump at a nominal flow rate of 0.3 Lpm.

3.3 Particle-phase Hg is collected using a glass-fiber filter in an open-faced Teflon® filter pack. Air is pulled through the particulate sampling system using a vacuum pump at a nominal flow rate of 30 Lpm.

3.4 Determination of vapor- and particle-phase mercury in ambient air is accomplished using cold-vapor atomic fluorescence spectrometry (CVAFS); more specifically, dual-amalgamation CVAFS. The amount of vapor-phase mercury collected on a gold-coated bead trap is determined directly by CVAFS. The sample trap is heated to release the collected mercury. The desorbed mercury is carried in an inert gas stream (He or Ar) to a second gold-coated bead trap, the analytical trap. The mercury collected on the analytical trap is then thermally desorbed and carried into the CVAFS analyzer. The resulting voltage peak is integrated to produce peak area for the sample.

3.5 Determination of Hg in the particle phase requires acid extraction of the glass-fiber filters prior to analysis. The sample filters are extracted in a nitric acid solution using microwave digestion to yield "acid-extractable" particulate mercury. The extract is oxidized with BrCl to convert all forms of Hg to Hg^{+2} and $SnCl_2$ is added to the extract to reduce the Hg^{+2} to volatile Hg^0 . The Hg^0 is liberated from the extract by purging with an inert gas (N_2) and collected on a gold-coated bead trap. The amount of mercury collected on the trap is then determined using dual-amalgamation CVAFS. The detection limits achieved using Method IO-5 are 30 pg/m^3 for particulate Hg and 45 pg/m^3 for vapor mercury.

4. Significance

4.1 The area of toxic air pollutants has been the subject of interest and concern for many years. Recently the use of receptor models has resolved the elemental composition of atmospheric aerosol into components related to emission sources. The assessment of human health impacts resulting in major decisions on control actions by federal, state, and local governments are based on these data.

4.2 Elemental mercury and most compounds of mercury are protoplasmic poisons and, therefore, may be lethal to all forms of living matter. In general, the organic mercury compounds are more toxic than mercury vapor or the inorganic compounds. Even small amounts of mercury vapor or many mercury compounds can produce mercury intoxication when inhaled by man. Acute mercury poisoning, which can be fatal or cause permanent damage to the nervous system, has resulted from inhalation of from 1,200 to 8,500 Fg/m^3 of mercury. The more common chronic poisoning (mercurialism) which also affects the nervous system is an

insidious form in which the patient may exhibit no well-defined symptoms for months or sometimes years after exposure. The symptoms usually associated with mercurialism are exaggerated emotional response, gingivitis, and muscular tremors. A person suffering from a mild case of mercury poisoning is usually unaware of the cause of the illness because the symptoms are psychopathological in nature. Likewise, these ambiguous symptoms may result in an incorrect diagnosis by a physician. In addition, animals and plants also exhibit a low tolerance to mercury and its compounds.

5. Definitions

5.1 Calibration--the process of correlating instrument response to known standard units of measure by regression analysis for the purpose of quantifying unknown samples based on observed instrument readings.

5.2 Calibration Standard--a solution prepared from a certified mercury standard stock solution which is used to calibrate instrument response to concentration.

5.3 Laboratory Duplicates (LD1 and LD2)--two aliquots of the same sample treated exactly the same throughout preparation and analysis. Analyses of laboratory duplicates provide an indication of precision associated with laboratory procedures.

5.4 Collocated Samples--samples collected from identical sampling systems placed in the field side-by-side. Collocated samples are collected and analyzed identically and are used to determine overall sampling and analytical precision.

5.5 Reagent Blank--the reagent blank is used to determine the amount of mercury added to samples from the laboratory reagents.

5.6 Field Blank (FB)--a field blank is treated exactly like an ambient sample during sample setup and removal, but air is not drawn through the field blank. The FB is used to determine the limit of detection and is site-specific.

5.7 Storage Blank (STB)--a blank created by storing either a gold-coated trap (vapor phase Hg), or a filter (particle phase Hg) prior to analysis. The STB is used to determine the amount of mercury added to samples during storage.

5.8 Mercury Standard Stock--a solution containing a certified concentration of mercury obtained from a commercial source (e.g., NIST-3133). This standard is used to prepare calibration standards.

5.9 Precision--a measure of the overall uncertainty in a particular measurement. Assessment of precision requires the analysis of collocated samples.

Precision is assessed using relative percent difference (RPD) between the collocated samples. The average precision is reported as the average of the absolute value of the RPD.

$$\text{RPD}' = \frac{(X_1 + X_2)(100)}{(X_1 - X_2)/2}$$

where:

X_1 = concentration from the first collector; and
 X_2 = concentration from the second collector.

5.10 Accuracy--a measure of the degree to which a measurement or computed value reflects the true value of analyte present. Accuracy is assessed using standard reference materials (SRM) that have been processed in a manner identical to the field samples.

Percent recovery, R, is used to assess accuracy from standard reference materials. Recovery is calculated as:

$$R = (\text{Measured Mass}/\text{Actual Mass})(100)$$

Certified reference materials for mercury in vapor and particulate phases are not available, preventing the assessment of accuracy in these media. Interlaboratory calibrations and sample exchanges are strongly recommended.

5.11 Detectability--the detection limit is defined as the lowest value of a characteristic that a measurement process, or a method-specific procedure can reliably discern. Three types of detection limits include the instrument detection limit (IDL), the method detection limit (MDL), and the system detection limit (SDL) defined as:

5.11.1 IDL. The smallest signal above background noise that an instrument can detect at a 99 percent confidence level. This value is quantified by direct injection of a spiked blank or other low level sample (1-5 times the theoretical IDL) into the instrument. The sample does not undergo any sample processing steps of the analytical methods and is used to provide the detection capabilities of the instrument.

5.11.2 MDL. The minimum concentration of a substance measured and reported with 99 percent confidence that the analyte concentration is greater than zero. This is determined from the analysis of a sample in a given matrix containing the analyte. It is essential that all sample processing steps of the analytical method be included in the determination of the MDL. In many cases the term "limit of detection" (LOD) and MDL are used synonymously.

5.11.3 SDL. The minimum concentration of analyte measured in a sample that is detectable and distinguishable from background noise of the entire data collection system. For Hg analyses, the SDL is defined as either the mean or 3F of the field blanks, whichever value is largest.

5.12 Completeness--The measure of the number of valid samples (meeting all QA requirements) obtained compared to the number required to achieve the objectives of the study. Overall completeness is the number of valid samples compared to the number planned. Laboratory completeness is the number of valid samples obtained compared to the number analyzed. As with the other data quality attributes, completeness can be controlled through adherence to analysis protocols in order to minimize contamination and sampling errors.

Completeness is calculated as:

$$\text{Completeness} = v/n(100)$$

where:

v = number of samples judged valid

n = total number of measurements necessary to achieve project objectives

6. Contamination

6.1 Determination of Hg in atmospheric samples requires the ability to reliably detect very small (picogram) amounts of mercury. The potential for contamination of ambient samples cannot be overemphasized.

6.2 Much of the effort required to obtain good data is associated with maintaining the cleanest possible conditions. Absolute adherence to clean techniques is essential throughout all phases of sample collection, handling, and analysis.

6.2.1 Class 100 Clean Room-A key element in minimizing exposure of samples to potential contaminants includes the use of a metal-free Class 100 clean room, which is supplied by HEPA filtered air that has been passed through charcoal adsorbent to reduce vapor-phase Hg levels. Procedures conducted in the clean room include the final stages of acid-cleaning for sample containers and supplies, the extraction and analysis of particulate mercury samples, and storage of ultra-pure reagents.

6.2.2 Preparation of Sampling Supplies to Minimize Contamination-All containers with which the sample comes into contact are acid-cleaned using the protocol described in this method. Supplies used to manufacture gold-coated traps for vapor-phase Hg collection and filters used for collection of particulate Hg are baked prior to use to volatilize Hg. Particle-free gloves are worn during all manipulations of sample containers and supplies. All acid-cleaned supplies are stored double or triple-bagged in resealable polyethylene. Containers for gold-coated bead traps and glass fiber filters prepared for sampling are sealed with Teflon® tape and bagged.

6.2.3 Minimizing Exposure During Sample Collection-On-site preparation of filters and traps for sampling is conducted by trained operators, outdoors to minimize potential particulate contributions. Sample preparation can also be performed indoors if a Class 100 environment is utilized. During all phases of sample set-up and removal, the operator wears particle-free gloves and stands downwind of the sample in order to prevent contamination by shedding particles from clothing or breathing on samples. After sampling, filters and traps are re-sealed in containers using Teflon® tape and bagged in resealable polyethylene.

6.2.4 Minimizing Exposure During Sample Analysis-All reagents utilized in the analysis of samples for Hg are highly purified to minimize Hg content. Suggested sources for low-Hg containing reagents are supplied in this method. Blank levels in reagents are carefully monitored and reagents are replaced periodically to maintain the lowest levels possible. Particle-free gloves are worn during all phases of sample analysis. Blanks from extraction vessels for particulate Hg analysis are monitored and analytical systems are maintained to insure consistent, low detection limits.

7. Interferences

7.1 Types of interferences and the procedures used to resolve them analytically vary depending on the manufacturer and model of the analytical instrument used. There are no known positive interferences at the wavelength of 253.7 nm used to excite and measure the fluorescence of Hg atoms using the CVAFS procedure as described. Suspected negative interferences include polyaromatic hydrocarbons and water vapor. Excessive water vapor will interfere by quenching the fluorescence signal as the Hg is liberated from the gold trap. Free halogens also present a hazard to the gold traps resulting in a permanent destruction of the trap resulting in low values or no response at all.

7.2 Ambient levels of dimethyl mercury, sulfur dioxide, hydrogen sulfide, and nitrogen dioxide do not interfere with the collection or analysis of mercury vapor when utilizing silver wool techniques. These compounds have not, however, been thoroughly tested utilizing the gold-coated bead trap technique. It is the users responsibility to evaluate these compounds when using this methodology.

8. Safety, Restrictions, and Limitations

8.1 The toxicity or carcinogenicity of reagents used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be available to all personnel involved in the chemical analysis.

8.2 Mercury compounds are highly toxic if inhaled, swallowed or absorbed through the skin. Laboratory personnel should use caution and wear gloves when handling standards containing mercury.

8.3 The American Conference of Governmental Industrial Hygienists (ACGIH) has adopted the threshold limit value (TLV) of 100 $\mu\text{g}/\text{m}^3$ for mercury vapor and inorganic compounds of mercury for an 8-hour work day. In addition, the ACGIH has established a TLV for organic mercury of 10 $\mu\text{g}/\text{m}^3$ for an 8-hour exposure.

9. Facilities, Equipment, and Materials

9.1 Facilities

9.1.1 Clean room-Class 100 with down-flow, positive pressure ventilation, and separated dressing room. Construction materials must be nonmetallic, preferably plastic or varnished wood attached without metal fasteners. Metal parts for which no substitute exists must be painted or otherwise sealed. Paints and varnishes must not contain mercury fungicides or additives. Non-permanent plastic enclosures which provide HEPA-filtered air at adequate flow rates can also, under many circumstances, provide an adequate clean environment. These facilities will likely require more strict adherence to maintenance and cleaning schedules.

9.1.1.1 Adhesive mats, for use at entry points and at work stations to remove dust and dirt from clean-room boots.

9.1.1.2 Laminar-flow exhaust hood for clean reagent preparation and particulate Hg sample processing and purging.

9.1.1.3 Clean room suit, hood, boots, and particle free gloves.

9.1.2 **Fume hoods** - for the acetone and hydrochloric acid soaking steps of the labware cleaning system.

9.2 Equipment

[Note: Following is a list of the required facilities, equipment, supplies and reagents for sample preparation, collection, and analysis. The make and model of some of the items are provided although many of the materials are available from a variety of sources.]

9.2.1 Mercury Analysis System

[Note: Separate CVAFS analysis systems dedicated to measurement of mercury from vapor phase and particulate samples is recommended since standardization procedures and analytical levels of Hg differ for the two media.]

9.2.1.1 Cold vapor atomic fluorescence spectrometer (CVAFS).

9.2.1.2 Power conditioner to reduce voltage fluctuations to CVAFS.

9.2.1.3 Integrator.

9.2.1.4 Variable voltage transformers (2) for thermally desorbing traps.

9.2.1.5 Mass flow controller for maintaining constant flow rate of carrier gas through CVAFS.

9.2.1.6 Four-channel programmable circuit controller.

9.2.1.7 Axial fans (2), 30 CFM, for cooling traps.

9.2.1.8 Nickel-chromium wire coils (2) for thermally desorbing gold traps.

9.2.2 Microwave Digestion System

9.2.2.1 Microwave oven equipped with temperature and pressure control system for extracting particulate Hg samples.

9.2.2.2 Teflon® digestion vessels.

9.2.3 **Muffle furnace**-for baking glass fiber filters, quartz wool, and quartz tubes; capable of heating to 700EC.

9.2.4 Pumps and Flow Measurement System

9.2.4.1 Sampling box (plastic enclosure, suitable for outdoor conditions, approximately 18x24").

9.2.4.2 Pole for sampling box (1-1/4" galvanized steel pipe nominally 10 feet long).

9.2.4.3 Mounting hardware for sampling box.

9.2.4.4 Vinyl tape to cover steel pipe and mounting hardware.

9.2.4.5 Trap heater, custom made.

9.2.4.6 Variable voltage transfer for trap heater.

9.2.4.7 Vacuum pumps, oil-less, brush-less, capable of flow rates of 30 Lpm and 0.3 Lpm with mass flow controller.

9.2.4.8 Rotameters, calibrated, capable of measuring 0.3 and 30 Lpm.

9.2.4.9 Dry test meter to measure total volume of air for particulate mercury sample.

9.2.5 Freezer for particulate Hg sample storage at -40EC.

9.3 Materials

9.3.1 Supplies for Cleaning Sampling and Analysis Equipment

- 9.3.1.1 Acetone, reagent grade.
- 9.3.1.2 Alkaline detergent.
- 9.3.1.3 Deionized water, high purity, 18.2 M S cm⁻¹.
- 9.3.1.4 Concentrated hydrochloric acid, trace metal grade.
- 9.3.1.5 Concentrated nitric acid, trace metal grade.
- 9.3.1.6 Water bath capable of maintaining temperature of 80EC.
- 9.3.1.7 Polyethylene or polypropylene tubs with lids, various sizes.
- 9.3.1.8 Polyethylene carboys, 20 L with spigot.
- 9.3.1.9 New, resealable polyethylene bags.
- 9.3.1.10 Particle-free wipes.

9.3.2 Supplies for Preparation of Gold-Coated Bead Traps

- 9.3.2.1 Sputter coater with 24 karat gold source.
- 9.3.2.2 Glass-blowing torch.
- 9.3.2.3 Tungsten rod for indenting quartz tubes.
- 9.3.2.4 Borosilicate glass beads (1 mm dia.), acid-washed.
- 9.3.2.5 Quartz tubes (10 cm length, 7 mm O.D., 5 mm I.D.).
- 9.3.2.6 Quartz wool.
- 9.3.2.7 Teflon® heat shrink tubing.
- 9.3.2.8 Teflon® end plugs, custom made.
- 9.3.2.9 Rigid plastic tubes with endcaps for gold trap storage.
- 9.3.2.10 Teflon® tape, ½”.
- 9.3.2.11 Polyethylene tube bags and heat sealer.

9.3.3 Supplies for Preparation of Glass Fiber Filters

- 9.3.3.1 Glass fiber filters, 47-mm.
- 9.3.3.2 Ceramic crucible.
- 9.3.3.3 Teflon® jars for storage of filters.
- 9.3.3.4 Teflon® tape, 1 in.

9.3.4 Supplies for Sample Collection

- 9.3.4.1 Teflon® filter holders, 47-mm, closed inlet for vapor-phase Hg, open inlet for particle-phase Hg.
- 9.3.4.2 Plastic petri dishes, 50 mm, for particulate mercury sample filters.
- 9.3.4.3 Plastic/sealable refrigerator type containers.
- 9.3.4.4 Teflon® coated forceps.
- 9.3.4.5 Particle-free gloves.
- 9.3.4.6 Resealable polyethylene bags.
- 9.3.4.7 Teflon® tape, 1” and ½”.
- 9.3.4.8 Teflon® tubing, ¼” O.D.
- 9.3.4.9 Latex tubing, 1/8” I.D.
- 9.3.4.10 Polyethylene tubing, 3/8” O.D.
- 9.3.4.11 Quick connectors.
- 9.3.4.12 Extension cords.

9.3.5 Supplies for Sample Analysis

- 9.3.5.1 Carrier gas, argon or helium, ultra-high purity (99.999%).
- 9.3.5.2 Purge gas, nitrogen, pre-purified (99.998%).
- 9.3.5.3 Gas tight syringe, 100 FL.
- 9.3.5.4 Injection port.
- 9.3.5.5 Minnert valve and septa for injection port.
- 9.3.5.6 Glass impinger and bubblers, 30 mL.
- 9.3.5.7 Pipets, including 1000 μL , 500 μL , 250 μL , 100 μL , and 50 μL .
- 9.3.5.8 Glass or Teflon[®] tubes, 1/2" O.D., 6" long, for soda lime traps
- 9.3.5.9 Teflon[®] reducing unions (1/2" to 1/4"), for connecting soda lime traps to bubbler exhaust and gold trap.
- 9.3.5.10 Concentrated nitric acid (HNO_3), highest purity.
- 9.3.5.11 Concentrated hydrochloric acid (HCl), highest purity.
- 9.3.5.12 Potassium bromide (KBr).
- 9.3.5.13 Potassium bromate (KBrO_3)
- 9.3.5.14 Hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$)
- 9.3.5.15 Stannous chloride dihydrate ($\text{SnCl}_2\cdot 2\text{H}_2\text{O}$).
- 9.3.5.16 1000 $\mu\text{g}/\text{mL}$ mercury standard, NIST-3133.
- 9.3.5.17 Elemental mercury, liquid, high purity.
- 9.3.5.18 Constant temperature ($\pm 0.1^\circ\text{C}$), circulating water bath.
- 9.3.5.19 Certified immersion thermometer.

10. Preparation of Supplies, Adsorbents and Reagents

10.1 Acid Cleaning Procedure

[Note: All Teflon® and polyethylene sample bottles, reagent bottles and analytical supplies which will come into contact with the samples are cleaned using the following procedures.]

[Note: The acids mentioned below may be reused many times. A large volume of each type of acid may be prepared and stored in dedicated polyethylene carboys. Acid should be checked for contamination or replaced regularly.]

10.1.1 Acetone Rinse-sampling and analytical supplies for acid-cleaning by first rinsing with reagent grade acetone in a fume hood.

10.1.2 Detergent Wash-supplies are then washed with a dilute Alconox detergent solution, rinsed five times with cold tap water followed by three rinses with deionized water.

10.1.3 Heated Hydrochloric Acid Soak-bottles are filled with 3M (250 mL of high purity concentrated HCl in 750 mL of D.I. water) trace metal grade HCl and soaked at 80°C in a water bath in a fume hood for six hours, then cooled to room temperature, emptied and rinsed three times with ASTM Type I water. Polyethylene or polypropylene tubs with lids are used to soak small items such as the filter packs, quartz tubes, Teflon® endplugs, etc.

10.1.4 Short Nitric Acid Soak-bottles and polyethylene tubs of small items are filled with 0.56M (35 mL of high purity HNO₃ diluted to 1,000 mL) trace metal grade HNO₃, soaked at room temperature for 72 hours, emptied, and rinsed three times with ASTM Type I water.

10.1.5 Long Nitric Acid Soak-bottles and covered tubs with supplies are transferred to the Class 100 clean room, rinsed three times with ASTM Type I water, and filled with 0.56 M HNO₃ and soaked at room temperature for 7 days. After the soaking period, the bottles & tubs are emptied and rinsed five times with ASTM Type I water.

10.1.6 Drying Step-all sampling and analytical supplies are dried in the clean room or in a Class 100 acrylic drying cabinet and double or triple bagged before being stored.

10.1.7 Bulk Nitric Acid Soak-supplies that cannot be heated in the HCl step are soaked in covered tubs with separately prepared 0.56M HNO₃ at room temperature for 7 days, rinsed and dried as described above.

10.2 Preparation of Gold-Coated Bead Traps

[Note: The following sections detail the steps for construction of gold-coated bead traps for collection of vapor-phase Hg in field studies. Depending upon the scope of the mercury sampling to be performed, it may be cost-effective to purchase traps or trap-making supplies from a commercial source.]

10.2.1 Preparation of Gold-Coated Beads and Trap

10.2.1.1 Borosilicate glass beads (1 mm diameter) are coated with a gold plasma generated under vacuum using a sputter coater. The thickness of the gold coating produced should be approximately 300 angstrom. The operating manual for the sputter coater should be consulted for the appropriate settings to obtain this thickness.

10.2.1.2 Quartz tubes are indented using a glass-blowing torch. Three radial indentations are made about 2.5 cm from one end of a 10 centimeter long tube.

10.2.1.3 All components of the gold bead traps are heated in a muffle furnace to remove any Hg prior to assembling traps. The gold-coated beads are baked at 500EC for one hour, the quartz wool at 600EC for one hour, and the quartz tubes at 700EC for one hour.

10.2.1.4 Teflon® heat-shrink tubing (0.25 in. diameter after shrinking), is cut into 1.25 in. pieces and acid cleaned with a bulk HNO₃ soak (see Section 10.1.7).

10.2.2 Construction of Trap

10.2.2.1 A small amount of quartz wool is rolled into a ball and placed in the quartz tube so that it rests on the indentations forming a short (~ 0.25 cm) plug. About 0.7 g of the gold-coated beads are added to the quartz tube on top of the quartz wool. A second ball of quartz wool is placed in the quartz tube so that it rests on top of the beads. Traps should be packed as tightly as possible without breaking the quartz wool fibers. Three more radial indentations in the quartz tube are made just beyond the second quartz wool plug.

[Note: Best results are obtained by maintaining the integrity of the quartz wool fibers when rolling and compacting the wool into the quartz tube. Also, loosely packed traps may result in air flowing around the beads and not contacting the gold surfaces.]

10.2.2.2 Teflon® heat-shrink tubing is attached to both ends of the trap so that about half of the tubing extends from the trap. The Teflon® endplugs are inserted into the Teflon® heat-shrink tubing.

10.2.2.3 Plastic tubes are used as storage containers for each individual trap with endplugs.

10.2.2.4 Each trap is labeled with a unique number to identify and monitor the performance of the trap.

10.2.3 Trap Conditioning and Testing

10.2.3.1 New traps are 'conditioned' prior to use by drawing air through the trap at 0.3 Lpm for 30 minutes and then 'blanked' by heating the trap to 500EC for five minutes while an inert gas (i.e., He) flows through the trap at 0.3 Lpm. The conditioning procedure is performed twice prior to testing the trap.

10.2.3.2 New traps are evaluated for their reproducibility in collecting vapor-phase Hg and for their blank levels prior to use.

10.2.3.3 Traps to be used in vapor-phase Hg sample collection are prepared by blanking the trap, Teflon®-taping the endplugs to the trap, placing the trap in the plastic storage tube, heat sealing the tube in polyethylene, then placing two gold traps for a sample in a resealable polyethylene bag.

10.3 Preparation of Glass Fiber Filters

[Note: Glass fiber filters used for collection of particle-phase Hg samples must be heated prior to use to release any Hg from the filter matrix.]

10.3.1 The glass fiber filters are placed in a clean crucible with a lid and heated in a muffle furnace at 500 EC for one hour.

10.3.2 After cooling for one hour in the muffle furnace but still hot, the filters are transferred from the crucible to an acid cleaned Teflon® jar (50 mm diameter) using acid cleaned Teflon® forceps. The lid to the Teflon® jar is sealed with Teflon® tape, and the jar is triple-bagged and stored in the clean room until needed.

10.3.3 Twenty percent of each batch of glass fiber filters used for particle-phase Hg samples and blanks are kept for preparation of standard addition filters used for CVAFS instrument calibration as described in Section 12.6.2.

11. Collection of Ambient Air Samples

[Note: A basic concern regarding sample collection is the potential for contamination. Absolute adherence to clean sampling protocols is essential. This includes, but is not limited to: (1) all supplies with which samples come into contact must be acid cleaned, (2) all sample containers must be handled with particle-free gloved hands at all times, (3) all sample containers must be bagged before and after sample collection, and (4) the operator must stand downwind of the sample during all phases of sample installation and removal.

In addition, all sample collection procedures (i.e. loading filters into filter packs) should be conducted outdoors (in the case that a Class 100 laboratory is unavailable on-site). If atmospheric mercury sampling is to be performed in locations that experience extreme weather conditions, additional measures can be taken to provide a 'clean' environment indoors for sample handling. Small laminar-flow hoods in site trailers have been used with good results for loading and unloading sample filters from filter packs.

This section describes the methods for collection of vapor and particle phase Hg samples. The configuration of the sampling equipment is described first followed by the specific procedures for collection of vapor and particle phase Hg, respectively. In the following, the term 'gold trap' is used to refer to traps made from gold-coated beads, gold-coated sand and/or a solid gold matrix which have been shown to produce equivalent results.]

11.1 The Sampling Equipment

11.1.1 The pumps used for collection of mercury samples in ambient air should be specially designed for trace-level pollutant sampling. High efficiency oilless, brushless pumps should be used and protected from weather (i.e., the pump housing should be well sealed from rain, insulated and heated during the winter, and fan cooled during the summer).

11.1.2 A fiberglass enclosure is used as the 'sample box' to house the filter packs and gold traps during sample collection (see Figure 1).

11.1.3 The box is mounted on a pole or tower at least 3 meters above ground level. Galvanized steel provides sufficient strength to support the sample box in high winds and may be wrapped with vinyl tape to prevent contamination from the metal surface.

11.1.4 Polyethylene tubing with quick connect couplings are used to connect the vacuum lines from the pump to the sample box.

11.1.5 For particle-phase mercury, a dry test meter (DTM) is connected to the vacuum line between the pump and the sample box for direct measurement of the volume of air sampled (in L).

11.1.6 Inside the sample box flexible latex tubing with quick connect couplings are used to connect the vacuum lines to the filter packs for particle-phase Hg. For vapor-phase Hg a piece of Teflon® tubing is attached to the end of the flexible latex tubing for connecting to the gold traps during sampling.

11.1.7 Moisture on gold surface interferes with the amalgamation of Hg. Therefore, condensation during collection of vapor-phase Hg must be prevented. To prevent condensation in the gold traps during sampling, a heat tube is used to keep the traps above ambient temperature. The heat tube is constructed from heat tape wrapped around a metal tube, insulated and covered with heat-shrink electrical tubing and electrical tape. The heat tube assembly is plugged into a variable voltage transformer to provide constant low heat to warm the trap.

11.1.8 The 47-mm Teflon® filter packs used for collection of vapor- and particle phase Hg are an assemblage of three main components—a threaded inlet, a filter support base with ¼ inch tube ferrule nut, and a clampdown nut to connect the inlet to the filter holder. For vapor-phase Hg a closed inlet filter pack with approximately 4” of ¼ inch Teflon® tubing is used to extend the air inlet several inches from the bottom of the sample box. For particle phase Hg an open inlet filter pack is used that protrudes several inches through the sample box during sampling and a plastic quick connect coupling is used for connection of the outlet to the vacuum line.

11.1.9 Rotameters calibrated for 0.3 and 30 Lpm are used initially to set the flow rate for vapor and particle-phase Hg respectively. To prevent potential contamination of the sample by the rotameter, separate ‘flow check’ filter packs are attached to the rotameters for this procedure. The flow check filter packs have closed inlets with quick connect couplings on the inlet tubing for connection to the rotameter.

11.1.10 A field test data sheet (FTDS) is used to record all field activities.

11.2 Collection of Vapor Phase Hg Samples

[Note: Collection of vapor-phase mercury in ambient air takes advantage of the amalgamating property of mercury to a gold surface. The amalgamation process requires a low flow rate to allow adsorption of the mercury in the air to the gold surface of the trap. A nominal flow rate of 0.3 Lpm is used to collect vapor phase Hg onto gold traps. A mass flow controller is employed to ensure a constant flow rate throughout the sampling period and the flow rate is checked both at the beginning and at the end of the sampling period with a calibrated rotameter. The volume of air sampled is determined from the average of the flow rate measurements and the sample duration. Checks of the flow rate also test for leaks and obstructions in the vacuum lines.]

Vapor phase Hg samples are collected using two gold traps in series as a quality control measure. The outlet from the first trap (‘A’ or ‘sample’ trap) is connected to the inlet of the second trap (‘B’ or ‘back’ trap) using Teflon® tubing. Any breakthrough from the first trap is collected on the second trap. The two traps are attached to a Teflon® filter pack containing a glass fiber filter to prevent intrusion of particulate matter into the gold traps.

11.2.1 Flow check procedure

11.2.1.1 The flow rate through the gold traps is set to 0.3 Lpm before each sample event using a rotameter calibrated for 0.3 Lpm. To prevent potential contamination of the sample by the rotameter, a separate flow check filter pack and gold trap are attached to the rotameter for this procedure. The flow check glass fiber filter should be replaced regularly but may be reused several times.

11.2.1.2 The sampling pump is allowed to warm up for at least 15 minutes prior to any flow measurement and/or adjustment.

11.2.1.3 The flow check filter pack and gold trap are placed in the sampling box and the vacuum line connected to the gold trap. The rotameter is connected to the inlet of the filter pack. After the system has been allowed to stabilize, the flow rate is adjusted to 0.3 Lpm and is recorded on the FTDS. The rotameter is disconnected from the filter pack and the gold trap disconnected from the vacuum line. The flow check filter pack and gold traps are removed from the sampling box.

11.2.2 Sample installation procedure

[Note: During all phases of sample set-up and removal, the operator stands downwind of the sample in order to prevent contamination by shedding particles from clothing, etc. In addition, particle-free gloves are worn when handling gold bead traps and prefilters.]

11.2.2.1 An acid cleaned 'sample' filter pack with closed inlet is loaded with a pre-fired glass fiber filter for each new vapor phase Hg sample to be collected and placed in the sample box.

11.2.2.2 The gold traps are taken from their plastic storage tubes and the endplugs removed.

11.2.2.3 The 'A' trap is connected to the Teflon® tubing from the outlet of the filter pack. A short piece of acid-cleaned Teflon® tubing is placed in the outlet of the 'A' trap. The 'B' trap is then attached to the Teflon® tubing.

11.2.2.4 The heat tube assembly is positioned to cover the 'A' trap.

11.2.2.5 To begin the sample, the Teflon® tubing at the end of the vacuum line is attached to the outlet of the 'B' trap.

11.2.2.6 Record the following parameters on the Hg FTDS: date, sampling location, time, ambient temperature, barometric pressure, relative humidity, mass flow control reading, rotameter reading, and gold-trap number. A typical Hg FTDS is documented in Figure 2.

11.2.2.7 Allow the sampler to operate for the desired time. At the end of the sampling period, record the parameters listed in Section 11.2.2.6. If the flows at the beginning and end of the sampling period differ by more than 10 percent, mark the gold-trap cartridge as suspect.

11.2.2.8 Calculate and record the average sample rate for the gold-trap cartridge according to the following equation:

$$Q_a = \frac{Q_1 + Q_2}{N}$$

where:

Q_a = Average flow rate in L/minute.

Q_1, Q_2 = Flow rates determined at beginning and end points during sampling.

N = Number of points averaged.

11.2.2.9 Calculate and record the total volumetric flow for the gold-trap cartridge using the following equation:

$$V_m = \frac{(T)(Q_a)}{1,000}$$

where:

V_m = Total volume sampled (m^3) at measured temperature and pressure.

T = Sampling time = $T_2 - T_1$, minutes

T_2 = Stop time.

T_1 = Start time.

11.2.2.10 The total volume (V_s) at standard conditions, 25EC and 760 mmHg, is calculated from the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273 + t_A}$$

where:

V_s = Total sample volume (m^3) at standard conditions, 25EC and 760 mmHg.

P_A = Average barometric pressure, mmHg.

t_A = Average ambient temperature, EC.

11.2.3 Sample recovery procedure

[Note: Particle-free gloves are worn during this procedure.]

11.2.3.1 The gold-traps are removed from the sampling box and the endplugs are replaced. The endplugs are sealed to the traps with Teflon® tape and the traps are returned to their respective plastic tubes and capped.

11.2.3.2 Labels with unique sample identification numbers are affixed to each tube. The tubes are sealed in polyethylene bags and returned to the laboratory for analysis.

11.2.3.3 The flow rate is checked after removal of the sample traps and filter pack using the procedure previously described in Section 11.2.1. The flow rate and any deviations from the standard operating procedures during removal of the sample must be recorded on the Hg FTDS.

11.2.3.4 The pump is turned off and the glass fiber prefilter is discarded. The Teflon® tubing connector should be returned to the laboratory for cleaning.

11.3 Collection of Particulate Hg Samples

[Note: Since particulate Hg occurs at ultra-trace levels in the atmosphere and Hg has a high vapor pressure, the selection of sampling flow rate and duration must be carefully considered. It is typically necessary to sample at a flow rate of 30 Lpm for 12-24 hours to collect enough particulate Hg for analysis. The volume of air sampled is measured directly using a calibrated dry test meter (DTM). In addition, the flow rate is checked both at the beginning and at the end of the sampling period with a calibrated rotameter to check for leaks or obstructions in the vacuum lines.]

11.3.1 Flow check procedure

11.3.1.1 The flow rate is checked before each sample event using a rotameter calibrated in the range of 30 Lpm. To prevent potential contamination of the sample by the rotameter, a separate flow check filter pack is attached to the rotameter for this procedure. The flow check glass fiber filter should be replaced regularly but may be reused several times.

11.3.1.2 The sampling pump is allowed to warm up for at least 15 minutes prior to any flow measurement and/or adjustment.

11.3.1.3 The flow check filter pack is placed in the sampling box. The outlet is connected to the vacuum line and the inlet to the rotameter. After the system has been allowed to stabilize, the flow rate is

adjusted to 30 Lpm and is recorded on the FTDS. The flow check filter pack is then disconnected from the rotameter and vacuum line, and removed from the sampling box.

11.3.2 Sample installation procedure

[Note: During all phases of sample set-up and removal, the operator stands downwind of the sample in order to prevent contamination by shedding particles from clothing, etc. In addition, particle-free gloves are worn when handling gold bead traps and prefilters.]

11.3.2.1 An acid cleaned 'sample' filter pack with open cylinder inlet is loaded with a pre-baked glass fiber filter with the 'fibrous side' up, touching only the edge of the filter with a pair of acid cleaned Teflon® coated forceps. The filter pack is placed in the sample box.

11.3.2.2 To begin the sample, the vacuum line is connected to the outlet of the sample filter pack.

11.3.2.3 Record the following parameters on the Hg Field Test Data Sheet (FTDS): date, sampling location, time, ambient temperature, barometric pressure, relative humidity, dry gas meter reading, rotameter reading (if applicable), gold-trap number and dry gas meter serial number. A typical Hg FTDS is documented in Figure 2.

11.3.2.4 Allow the sampler to operate for the desired time. At the end of the sampling period, record the parameters listed in Section 11.3.2.3. If the flows at the beginning and end of the sampling period differ by more than 10 percent, mark the filter cartridge as suspect.

11.3.2.5 Calculate and record the average sample rate for the filter cartridge according to the following equation:

$$Q_a = \frac{Q_1 + Q_2}{N}$$

where:

- Q_a = Average flow rate in L/minute.
- Q_1, Q_2 = Flow rates determined at beginning and end points during sampling.
- N = Number of points averaged.

11.3.2.6 Calculate and record the total volumetric flow for the gold-trap cartridge using the following equation:

$$V_m = \frac{(T)(Q_a)}{1,000}$$

where:

- V_m = Total volume sampled (m^3) at measured temperature and pressure.
- T = Sampling time = $T_2 - T_1$, minutes
- T_2 = Stop time.
- T_1 = Start time.

11.3.2.7 The total volume (V_s) at standard conditions, 25EC and 760 mmHg, is calculated from the following equation:

$$V_s = V_m \times \frac{P_A}{760} \times \frac{298}{273 + t_A}$$

where:

V_s = Total sample volume (m^3) at standard conditions, 25EC and 760 mmHg.

P_A = Average barometric pressure (mmHg) during sampling.

t_A = Average ambient temperature (EC) during sampling.

11.3.3 Sample recovery procedure

[Note: Particle-free gloves are worn during this procedure.]

11.3.3.1 The sample filter is removed from the filter pack and placed in an acid cleaned petri dish using acid-cleaned Teflon®-coated forceps, touching only the edge of the filter.

11.3.3.2 The petri dish is sealed with Teflon® tape and a label with a unique sample identification number is affixed to the cover of the petri dish. The petri dish is double bagged and returned to the laboratory for analysis.

11.3.3.3 The flow rate is checked after removal of the sample Hg traps using the procedure previously described in Section 11.3.1. The flow rate and any deviations from the standard operating procedures during removal of the sample must be recorded on the Hg FTDS.

11.4 Sample Storage

11.4.1 Vapor-phase Hg samples can be stored up to one week at 4EC until analyzed.

11.4.2 Particle-phase Hg filters can be stored indefinitely in a freezer at -40EC until analyzed.

12. Analysis of Ambient Air Samples

12.1 Introduction

12.1.1 This section describes the methods for analysis of vapor and particle phase Hg samples. Dual-amalgamation cold vapor atomic fluorescence spectrometry (CVAFS) is used to determine the amount of Hg collected for both types of samples.

12.1.2 The analytical system is described first followed by the specific procedures for analysis of vapor and particle phase Hg, respectively.

[Note: In the following, the term 'gold trap' is used to refer to traps made from gold-coated beads, gold-coated sand and/or a solid gold matrix which have been shown to produce equivalent results.]

12.2 The Analytical System

12.2.1 The analytical system consists of a pair of gold traps in series, a thermal desorption system, a CVAFS mercury detector, an integrator to convert peak voltage to peak area, and an inert carrier gas (He or Ar).

12.2.2 The dual-amalgamation technique requires two gold traps in series: a 'sample' trap and an 'analytical' trap. This technique has two main advantages: it virtually eliminates interferences due to organics and Cl₂ from the sample trap and provides greater analytical precision because the same analytical trap is being used to introduce the Hg into the detector for all the samples.

12.2.3 The thermal desorption system includes a pair of nickel-chromium coils each with a variable transformer to regulate the output, a pair of small axial fans to cool the coils and traps quickly, and a programmable circuit controller to coordinate the trap heating and cooling cycles.

12.2.4 Power supplied to the CVAFS should be stabilized by a power conditioner to reduce line voltage fluctuations. The instrument is left on continuously to stabilize the UV lamp and maintain consistency from one day to the next. Operating manuals for the CVAFS instruments describe in detail the operation and maintenance for the specific analyzer.

12.2.5 The carrier gas should be mass-flow controlled to produce a more consistent peak response. Ultra-high purity gas should be used and a gold trap placed upstream of the sample and analytical traps to remove any remaining traces of Hg in the gas.

12.2.6 The vapor phase Hg analytical system requires an injection port and gas-tight syringe (100 FL) to introduce Hg standards into the sample train.

12.2.6.1 A small amount (2-3 mL) of liquid metallic Hg in a closed 150 mL flask is sufficient to generate Hg saturated air above the liquid surface for vapor-phase Hg analysis. The flask is immersed in a constant temperature ($\pm 0.1^\circ\text{C}$) circulating water bath. A certified immersion thermometer should be used to monitor the temperature of the air above the mercury in the flask. The temperature of the air in the flask must be maintained below room temperature otherwise, the Hg will condense on the walls of the injection apparatus.

12.2.6.2 The gas-tight 100 FL syringe should rest on top of the flask with the needle portion protruding through a Minnert valve into the flask air. Hg saturated air from the flask should be drawn up into the syringe and allowed to equilibrate.

12.2.6.3 An injection port with Minnert valve and Teflon-coated septum are used for injecting Hg saturated air onto gold traps in the analytical system. The port is placed inline for the calibration process and then removed.

12.2.6.4 Vapor phase analysis is done outside of the clean room.

12.2.7 The particle-phase Hg analytical system requires an aqueous purging system which consists of: (i) an acid cleaned glass impinger and bubbler system (30 mL capacity) with Teflon® stopcock, (ii) a soda lime trap to capture acid gases from the bubbling solution, (iii) gold traps for collection of volatilized Hg from the extracts, and (iv) N₂ carrier gas for the system.

12.3 Preparation of Reagents and Standards

12.3.1 Deionized water-Deionized water, with a resistivity of 18.2 MS cm, is prepared using a water purification system (e.g., Milli-Q) from a prepurified (reverse osmosis) water source. This purified water conforms to the standards for ASTM Type I water.

12.3.2 Hydrochloric acid-containing low concentrations of Hg are used to prepare BrCl and SnCl₂ solutions. EM Science SupraPur® HCl is recommended.

12.3.3 Bromine Monochloride-(BrCl) is made from high purity potassium bromide (EM Science) and potassium bromate (Baker). The bromine salts (10.8 g of KBr and 15.2 g of KBrO₃) are weighed using acid cleaned weigh boats and spatulas. In the clean room laminar flow exhaust hood, an acid cleaned magnetic stir bar is placed in a 1L glass bottle of concentrated, high purity HCl. The KBr is added while stirring the acid with a magnetic stir plate, and allowed to dissolve completely (approx. 1 hour). The KBrO₃ is then added slowly while stirring. After all of the salts have been added, the solution is allowed to mix until all visible particles have dissolved (1-2 hours). The solution should be deep yellow in color. If there is no color (or very faint) then the solution should be remade because the BrCl has undergone reduction and will not have sufficient strength to oxidize all mercury species to Hg⁺². The BrCl is stored at room temperature in the clean room exhaust fume hood.

[Caution: BrCl should always be prepared in an exhausting fume hood because hazardous chlorine (Cl₂) gas is produced.]

12.3.4 Hydroxylamine hydrochloride-(NH₂OH•HCl) solution is prepared by dissolving 75.0 g of NH₂OH•HCl (EM Science) in ASTM Type I water in an acid cleaned 250 mL volumetric flask. The solution is stored in an opaque Teflon® bottle and refrigerated when not being used.

12.3.5 Stannous chloride-(SnCl₂) solution is prepared by placing 200.0 g of SnCl₂•2H₂O (Fluka) in an acid cleaned 1000 mL volumetric flask. In the clean room laminar flow exhaust fume hood, 100 mL of concentrated, high purity HCl is slowly added. After most of the SnCl₂ has dissolved (it does not dissolve completely), the solution is brought up to volume with ASTM Type I water. The SnCl₂ solution is stored in an acid cleaned, opaque Teflon® bottle and refrigerated when not being used.

12.3.6 Working mercury standard-solution used for CVAFS instrument calibration is prepared by sequential dilution of a commercial primary standard of 1000 µg Hg/mL. A secondary standard with a concentration of 1000 ng Hg/mL is made by adding 100 µL of the primary standard and 5 mL of BrCl (see Section 12.3.3) to a 100 mL volumetric flask, and diluting to the 100 mL total volume with ASTM Type I water. The secondary standard solution is remade at least once per year. The working standard has a concentration of 2 ng Hg/mL in 1 percent BrCl and is prepared by adding 200 µL of the secondary standard and 1000 µL of BrCl to a 100 mL volumetric flask and diluting to 100 mL total volume with ASTM Type I water. All standard solutions are stored in the dark at 5°C.

12.3.7 Nitric acid-(HNO₃) extraction solution (10% HNO₃, 1.6 M) is used for microwave digestion of particulate Hg samples. In the clean room laminar-flow exhausting hood 100 mL of high purity concentrated HNO₃ (EM Science SupraPur®) is slowly added to 750 mL of ASTM Type I water in a 1000 mL volumetric flask. The solution is mixed, allowed to cool, and brought up to 1000 mL with ASTM Type 1 water. The extraction solution is stored in an acid cleaned repipetting bottle in the clean room exhaust hood.

12.4 Summary of Dual-amalgamation CVAFS Analytical Procedure

12.4.1 The analytical procedure for detection of mercury using CVAFS includes three main steps.

12.4.2 First, the sample trap is placed in the analytical system and heated to release the collected mercury. The released mercury is entrained by the gas stream, carried into the analytical trap where it is amalgamated to the gold surface. Second, the analytical trap is heated to release the mercury which then flows into the CVAFS detector cell. Third, the mercury in the detector cell absorbs UV light and the resulting fluorescence is converted to a voltage proportional to the amount of Hg detected by a photomultiplier tube.

12.4.3 An integrator then converts the voltage response to peak area.

12.5 Analysis of Vapor Phase Hg Samples

12.5.1 Injection system calibration

12.5.1.1 The injection system is conditioned before each day of analysis to ensure precise and reproducible results. The process includes the following steps: (i) condition the syringe by flushing it three times with Hg saturated air, filling it to capacity, and allowing it to equilibrate for 15 minutes, (ii) place a new septum in the injection port and condition them both with multiple injections of Hg saturated air before initiating calibration.

12.5.1.2 The flask should be periodically flushed (approx. once per month) with pre-filtered N₂ gas in order to displace any oxygen which may oxidize the surface of the liquid mercury and prevent volatilization. Also, the Minnert valve for the syringe on the flask should be above the level of the water in the water bath. If water gets into the flask, it should be purged as described above.

12.5.2 CVAFS instrument calibration

12.5.2.1 A calibration curve, generated by injection of different volumes of Hg saturated air onto a gold trap, must be performed before each analysis. The amounts of Hg injected for the calibration curve should be tailored to the expected value of the samples to be analyzed. Table 1 shows an example calibration curve for 24 hour vapor-phase Hg samples consisting of five different amounts of Hg injected: 0, 0.2, 0.4, 0.8 and 1.6 ng of Hg.

12.5.2.2 To generate standard injections for the calibration curve, the conditioned injection port is placed in the analytical train in front of the gold trap to be used for generating the standard curve (called the "standard trap"). A specified volume of Hg saturated air is withdrawn from the flask using the gas tight syringe and injected onto the blanked standard trap through the injection port valve. After the injection the syringe is returned to the flask and filled to capacity until the next injection. The temperature of the air in the flask is recorded for each injection to calculate the actual amount of Hg injected.

12.5.2.3 A calibration curve is performed beginning with a zero point (0 FL) and continuing in ascending order to the highest amount. The zero point of the calibration curve is generated in the same manner described above except that no Hg saturated air is injected into the port. The amount of Hg emitted from the needle tip and the injection apparatus and adsorbed onto the gold trap is called the zero point (typically between 1-5 pg Hg).

12.5.2.4 The response for each standard injection is obtained by dual-amalgamation CVAFS described in Section 12.2.

12.5.2.5 At any given temperature the vapor density of Hg can be calculated using the Ideal Gas Law and the saturation vapor pressure of Hg. A table of vapor densities versus temperature is used to determine the amount of Hg injected for the volume of each standard injection. Table 1 illustrates the amount of Hg delivered during a typical injection procedure used to generate a standard curve at a flask temperature of 16.6EC.

12.5.2.6 The slope of the calibration curve is calculated using linear regression. The 0 FL injection response is subtracted from each of the points on the curve. The CVAFS analytical system is linear and the coefficient of determination (r^2) should be 0.999 or better and each of the points on the curve should be predicted by the slope within 5 percent of their actual value. If these criteria are not met, the specific points that are errant should be repeated and the linear regression recalculated.

12.5.2.7 The injection port and standard trap are removed from the analytical train after calibration.

12.5.3 Sample Analysis

12.5.3.1 After a satisfactory calibration curve for the CVAFS is obtained, sample traps are analyzed by dual amalgamation CVAFS as described in Section 12.2.

12.5.3.2 Control standards should be analyzed at regular intervals during the analysis of samples to detect any drift in the response or change in sensitivity of the CVAFS instrument. Control standards are generated in the same manner as the calibration standards described above. The volume of Hg saturated air injected for a control standard should be representative of the Hg concentration of the samples being analyzed.

12.5.3.3 The predicted value of the control standards should be within 5% of the calibration curve before continuing to analyze samples. If subsequent control standards also deviate by more than 5% from the calibration curve, it is likely that the analyzer sensitivity has changed and a second calibration curve should be generated. Sample analysis should only continue after recalibration has met the criteria outlined in 12.5.2.6.

12.6 Analysis of Hg in Particulate Samples

12.6.1 Microwave Digestion System

12.6.1.1 The use of microwave digestion to extract samples for analysis allows rapid heating and elevated pressures for shorter preparation time in a safer and more consistent manner compared to traditional procedures.

12.6.1.2 The microwave digestion system must use Teflon® vessels and be capable of monitoring and controlling pressure and temperature inside the vessels.

12.6.1.3 The microwave should be programmable for the target pressure and temperature, and for maintaining them for a specified time. The operating manual for the microwave digester should be consulted for programming, safety and maintenance of this equipment.

12.6.2 Preparation of Standard Addition and Sample Filters for Extraction

[Note: All preparation of filters for particulate Hg analysis must be performed in a Class 100 clean room. Filters are removed from storage in a -40EC freezer and allowed to equilibrate to room temperature in the clean room. Acid-cleaned Teflon® microwave vessels and Teflon®-coated forceps are needed for the filter preparation. Calibration standards using filter media are prepared at the same time as the sample filters to be analyzed. The microwave vessels should be labeled with the appropriate identifier for the contents of each vessel.]

12.6.2.1 Glass fiber filters heated and stored with the sample filters as described in Section 10.3 are used as standard addition filters for calibration of the CVAFS instrument. In the clean room, the standard filters are placed into acid cleaned microwave vessels using acid cleaned Teflon®-coated forceps. The filters are spiked with appropriate volumes of the 2 ng/mL Hg working standard to generate a calibration curve. Table 2 shows the volume of Hg standard added to the filters in the microwave vessels to produce a typical calibration curve for 24 hour particulate Hg samples. The Hg working standard solution is pipetted directly onto the filter and absorbed by the filter.

12.6.2.2 All sample filters to be analyzed should be prepared at the same time and handled identically according to the following procedures. Each petri dish containing a sample filter is removed from the sealed polyethylene bag and the Teflon® tape around the dish removed and discarded. The filter is removed from the petri dish using acid cleaned Teflon®-coated forceps touching only the edge of the filter to avoid the center area with the collected particulate matter. The filter is carefully folded into quarters using two pairs of forceps and placed into the appropriately labeled vessel. The forceps are cleaned after touching each sample filter by rinsing the tips in acid cleaned glass beakers of 10% HNO₃ extraction solution and ASTM Type I water.

12.6.3 Filter Extraction using Microwave Digestion

[Note: The prepared standard and sample filters are handled identically using the following microwave extraction procedure.]

12.6.3.1 In the clean room exhaust hood, the extraction solution (10% HNO₃, 1.6 M) should be prepared as described in Section 12.3. A calibrated repipettor is used to dispense 20 mL of extraction solution into each vessel.

12.6.3.2 Each vessel should be weighed both prior to and following the microwave digestion to ensure no loss of sample extract during the procedure.

12.6.3.3 The prepared vessels can then be removed from the clean room and placed in the microwave oven for digestion. The pressure and temperature monitoring sensors should be appropriately attached and the control program initiated. Optimal results for digestion of glass fiber filters for mercury determination have been obtained by heating the samples at 160EC and 70 psi for 20 minutes.

12.6.3.4 After the microwave digestion procedure is complete, the vessels should be allowed to cool until the pressure inside the control vessel is about 1-2 psi. then removed from the microwave and returned to the clean room.

12.6.4 Oxidation of Digested Filters

12.6.4.1 In the clean room exhaust hood, the vessels are opened carefully and 0.5 mL of BrCl (see Section 12.3.3) is added to the extract in each vessel to oxidize all of the mercury in solution to Hg²⁺.

12.6.4.2 The capped vessels are gently swirled to mix the vessel contents and allowed to react for a least 1 hour.

12.6.5 Aqueous Purging System

[Note: In the clean room exhaust hood an aqueous purging system is used to volatilize HgE from the filter extraction solution onto gold traps for quantification by CVAFS. The flow rate of the carrier gas through the purging system should be maintained at 0.5 Lpm.]

12.6.5.1 A soda lime trap is made from an acid cleaned borosilicate glass tube (15 cm long, 15 mm outer diameter) or from Teflon® tubing of similar dimensions. Acid cleaned Teflon® tubing and compression fittings are used to attach the trap to the impinger exhaust.

12.6.5.2 Before beginning analysis the tube is packed with high purity grade soda lime using a small amount of glass wool (1/2") as endplugs. The soda lime trap is then conditioned by purging 20 mL of a 5% HCl solution (0.3 M) for 30 minutes.

12.6.5.3 Purging solution is prepared by adding 1 mL SnCl₂ (Section 12.3.5) to 20 mL of ASTM Type I water in a bubbler and purging for 15 minutes to remove any Hg in the solution or purging system.

12.6.6 Volatilization and Recapture Procedure

[Note: The following volatilization and recapture procedure is used to liberate HgE from the oxidized filter extracts and collect it on gold traps for quantification by CVAFS.]

12.6.6.1 A 5 mL aliquot of the oxidized filter extract is pipetted from the Teflon® vessel into 20 mL of the bubbling solution prepared above.

12.6.6.2 To reduce the halogens in the extract, 0.1 mL NH₂OH•HCl (see Section 12.3.4) is pipetted into the bubbler. The bubbler is swirled briefly to mix the solution and allowed to react for 5 minutes.

12.6.6.3 A blanked gold trap is attached to the end of the soda lime trap connected to the impinger for collection of mercury from the bubbled solution.

12.6.6.4 To reduce the oxidized mercury in solution to volatile HgE, 0.5 mL SnCl₂ is pipetted into the bubbler which is immediately attached to the impinger and purged onto the gold trap for 7 minutes.

12.6.7 CVAFS Instrument Calibration using Standard Addition Filters

12.6.7.1 A calibration curve, generated using the standard addition filter extracts, must be performed before each analysis. A calibration curve is performed beginning with the reagent blank (no Hg standard added to filter) and continuing in ascending order to the highest concentration standard.

12.6.7.2 The volatilization and recapture procedure described in Section 12.6.6 is used to collect the Hg in solution for each standard addition filter onto gold traps. The amount of Hg volatilized from the extracts is determined by analysis of the gold trap using dual-amalgamation CVAFS as described in Section 12.4.

12.6.7.3 The concentration of Hg in the extraction solution for each of the standard addition filters is determined from the amount of 2 ng/mL mercury standard added to the filter, the total volume of reagents added, and the volume of solution analyzed. The actual amount of mercury in 5 mL of standard filter extracts are as shown in Table 2.

12.6.7.4 The slope of the calibration curve is calculated using linear regression. The reagent blank response is subtracted from each of the points on the curve. The CVAFS analytical system is linear and the coefficient of determination (r²) should be 0.99 or better and each of the points on the curve should be predicted by the slope within 10% of their actual value. If these criteria are not met, the specific points that are errant should be repeated and the linear regression recalculated.

12.6.8 Sample Analysis

12.6.8.1 After a satisfactory calibration curve for the CVAFS is obtained using standard addition filter extracts, Hg in each sample filter extract is volatilized and recaptured using the procedure described in Section 12.6.2.

12.6.8.2 The gold traps are analyzed by dual amalgamation CVAFS as described in Section 12.4 to quantify the amount of Hg in the sample filter extract.

12.6.8.3 Control standards should be analyzed at regular intervals during the analysis of samples to detect any drift in the response or change in sensitivity of the CVAFS instrument. Control standards are generated in the same manner as the calibration standards described above. The standard addition filter used for a control standard should be representative of the Hg concentration of the samples being analyzed.

12.6.8.4 The control standards response should be within 10% of the calibration curve before continuing to analyze samples. If subsequent control standards also deviate by more than 10% from the calibration curve, it is likely that the analyzer sensitivity has changed and a second calibration curve should be generated. Sample analysis should continue after recalibration.

13. Calculation of Mercury Concentrations in Ambient Air

13.1 Calculation of Vapor Phase Mercury Concentrations

13.1.1 Conversion of vapor phase mercury analysis results to ambient concentrations requires the results from analysis (samples, blanks and calibration curve) and flow rate and duration data from field logs. For example calculations see Section 13.1.2.

13.1.1.1 Vapor phase mercury concentrations in ambient air are reported in ng/m³.

13.1.1.2 The amount of mercury collected on a Au-coated bead sample trap (ng Hg) is calculated from the integrator response for the sample [in Peak Area Units (PAU)] multiplied by the slope of the calibration curve, which is in ng Hg/PAU.

13.1.1.3 The amount of mercury collected on a Au-coated bead sample trap is blank corrected by subtracting the average amount of mercury collected on field blank traps. Field blanks are described in Section 14.2.2.

13.1.1.4 Vapor phase mercury samples are typically collected using 2 Au-coated bead sample traps in series (the exit from the first trap is connected to the inlet of the second trap). The total amount of Hg collected for the sample is then calculated by simple addition of the blank corrected amounts of mercury from the two sample traps.

13.1.1.5 The volume (m³) of air sampled is calculated by multiplying the flow rate through the sample traps (in cm³/min.) by the duration of the sample (min.) and converting the product from cm³ to m³.

13.1.1.6 The ambient vapor phase mercury concentration in ng Hg/m³ is calculated from the total blank corrected ng of Hg for the sample traps divided by the cubic meters of air sampled.

13.1.2 Example Calculation of Ambient Vapor Phase Mercury Concentration

13.1.2.1 An example vapor phase mercury calibration curve is given in Table 3 and discussed in Section 12.5.2.

13.1.2.2 Calculation of the ng of Hg recovered from two sample traps in series:

Amount of Hg Recovered = Integrator Response x Slope of Calibration Curve

7,135,900 PAU x 1.0585E-7 ng Hg/PAU = 0.755 ng Hg

236,183 PAU x 1.0585E-7 ng Hg/PAU = 0.025 ng Hg

13.1.2.3 Calculation of the total ng of Hg for the sample:

Total Amount of Hg for sample = E (Sample, ng Hg - Average Field Blank, ng Hg)

(0.755 ng Hg - 0.015 ng Hg) + (0.025 ng Hg - 0.015 ng Hg) = 0.750 ng Hg

13.1.2.4 Calculation of the volume of air sampled at a flow rate of 0.3 Lpm and a sample duration of 24 hours, with average ambient temperature of 20EC and average barometric pressure of 750 mmHg:

Volume of Air Sampled = Flow Rate x Duration

(0.3 Lpm) (24 hr.) (1,440 min./24 hr.) (10^{-3} m³/L) = 0.432 m³

13.1.2.5 Correct total sample volume (m³) to standard conditions of 25°C and 760 mmHg:

$$\begin{aligned} V_s &= (V_m) \left(\frac{P_A}{760} \right) \left(\frac{298}{273 + t_A} \right) \\ &= (0.432 \text{ m}^3) \left(\frac{750}{760} \right) \left(\frac{298}{301} \right) \\ &= (0.432) (0.9868) (0.9900) \\ &= 0.422 \text{ m}^3 \text{ at standard temperature and pressure.} \end{aligned}$$

13.1.2.6 Calculation of the vapor phase mercury concentration (ng Hg/m³) for an ambient air sample at standard temperature and pressure:

Concentration = Total Amount of Hg for Sample / Standard Volume of Air Sampled

0.750 ng Hg / 0.422 m³ = 1.77 ng Hg/m³ at standard temperature and pressure.

13.2 Calculation of Particle-Phase Mercury Concentration

13.2.1 Conversion of particle-phase mercury analysis results to ambient concentrations requires the results from analysis (samples, blanks and calibration curve) and the volume of air sampled from field logs.

13.2.1.1 Particle-phase mercury concentrations in ambient air are reported in pg/m³.

13.2.1.2 The amount of mercury detected for the aliquot of sample analyzed is calculated from the integrator response [in Peak Area Units (PAU)] for the sample and the reagent blank. The difference between the sample and reagent blank integrator response is multiplied by the slope of the calibration curve, which is in pg Hg/ (PAU).

13.2.1.3 The amount of mercury collected on the entire sample filter is calculated by multiplying the amount of mercury in the aliquot by the ratio of the total extraction volume of 20.5 mL (20 mL of extraction solution and 0.5 mL of BrCl) to the volume of the aliquot analyzed (5 mL).

13.2.1.4 The volume (m³) of air drawn through the sample filter is calculated from the difference between the “on” and “off” readings for the Dry Test Meter (DTM) used to measure sample volume and adjusted by the calibration curve for the DTM display.

13.2.1.5 The particle-phase mercury concentration in pg/m³ is calculated from the amount of mercury collected on the filter divided by the cubic meters of air sampled.

13.2.2 Example Calculation of Ambient Particle-Phase Mercury Concentration

13.2.2.1 An example particle-phase mercury calibration curve is displayed in Table 4 and discussed in Section 12.6.7.

13.2.2.2 Calculation of the pg of Hg detected for the aliquot analyzed:

Amount of Hg Detected for Aliquot =
(Sample - Reagent Blank Integrator Response) x (Slope of Calibration Curve)

(7,135,900 PAU - 168,320 PAU) (9.1091E-5 pg Hg/PAU) = 635 pg Hg in aliquot.

13.2.2.3 Calculation of the pg of Hg for the entire sample filter:

Amount of Hg for Filter = (Amount of Hg for Aliquot) (Extraction Volume /Volume of Aliquot)

(635 pg Hg) (20.5 mL) / (5 mL) = 2604 pg Hg for filter

13.2.2.4 Calculation of the volume of air sampled from the DTM readings with average ambient temperature of 20EC and average barometric pressure of 750 mmHg during sampling:

Volume of Air Sampled = ("Off" - "On" DTM readings) x Slope of DTM Display Calibration
(1075.6 m³ - 1031.3 m³) x 0.975 = 43.2 m³

13.2.2.5 Correct total sample volume (m³) to standard conditions of 25EC and 760 mmHg:

$$\begin{aligned}
 V_s &= (V_m) \left(\frac{P_A}{760} \right) \left(\frac{298}{273 + t_A} \right) \\
 &= (43.2 \text{ m}^3) \left(\frac{750}{760} \right) \left(\frac{298}{301} \right) \\
 &= (43.2) (0.9868) (0.9900) \\
 &= 42.2 \text{ m}^3 \text{ at standard temperature and pressure.}
 \end{aligned}$$

13.2.2.6 Calculation of the particle-phase mercury concentration (pg Hg/m³) for an ambient air sample at standard temperature and pressure:

Concentration = [Amount of Hg for Filter - Avg. Field Blank]/ Volume of Air Sampled
2604 pg Hg / 42.2 m³ = 61.70 pg Hg/m³

14. Quality Assurance/Quality Control (QA/QC)

14.1 Personnel Qualifications

14.1.1 Field operators should be properly trained in the methods for ambient air sample collection as described in Section 11.

14.1.2 Field operators should routinely collect field blanks and shipping blanks to ensure that clean handling techniques are consistently employed.

14.1.3 Laboratory analysts should be properly trained in the procedures for analysis of ambient air samples as described in Section 12.

14.2 QA/QC Samples

14.2.1 Laboratory procedural blanks (LPB) are used to monitor the degree of background contamination introduced during the laboratory analysis procedures. For analysis of vapor and particle-phase Hg this blank is equivalent to the zero-point on the calibration curve and are analyzed before beginning analysis of samples.

14.2.2 Field Blanks

14.2.2.1 Field blanks are performed to determine the level of sample contamination during all phases of sample handling, including:

- Sample collection and handling in the field
- Shipment
- Storage
- Sample handling and analysis in the laboratory

14.2.2.2 Field blanks are performed using the same procedures as those described for collecting samples in Section 11. A minimum frequency of one field blank collected and analyzed per 10 samples is recommended for each sampling media. Field blank levels less than 2% of the average amount of mercury collected for a sample can be obtained using the methods described.

14.2.2.3 Vapor phase mercury field blanks are performed by placing the filter pack and attached gold bead trap in the sampling box as described for a sample, and left in the sample box for 2 minutes without the vacuum line attached. The vapor phase mercury field blank is removed from the sampling box as described for a sample and labeled appropriately.

14.2.2.4 Particle-phase mercury field blanks are performed by loading a glass fiber filter into the open-face filter pack as described for a sample. The filter pack is placed in the sampling box for 2 minutes without connecting it to the vacuum line. The particle-phase mercury field blank is removed from the filter pack as described for a sample and labeled appropriately.

14.2.3 Collocated Samples

14.2.3.1 Collocated samples are used to assess sample variability attributable to:

- Sample collection and handling in the field
- Shipment
- Storage
- Sample handling and analysis in the laboratory

14.2.3.2 Collocated sampling for a minimum of 1 per 20 samples collected is recommended to properly evaluate variability. Percent differences of less than 10% between collocated samples can be achieved using the methods described.

14.2.3.3 To collect collocated samples in the field, dual sets of sampling equipment must be used which are equivalent in all measurable ways.

14.2.4 Storage Blanks

14.2.4.1 Storage blanks are performed to determine the level of sample contamination during shipment and storage of samples, and therefore are only required when supplies and samples are shipped between a laboratory and a field site.

14.2.4.2 A minimum frequency of one storage blank collected and analyzed per 10 samples is recommended for each sampling media when samples are shipped to field sites.

14.2.4.3 Storage blank levels less than 1% of the average amount of mercury collected for a sample can be obtained using the methods described.

14.2.4.4 For a vapor phase mercury storage blank, a gold trap is sent to the field site and back to the laboratory for analysis without ever being opened in the field.

14.2.4.5 Particle-phase mercury storage blanks are performed by loading a glass fiber filter from the Teflon® storage jar directly into a plastic petri dish. The packaged filter is then sent to the field site and back to the laboratory for analysis, again without being opened.

14.3 Precision and Accuracy

14.3.1 Precision

14.3.1.1 Collocated samples can be used to assess the overall precision of the method (sampling and analytical precision). Precision of less than 15% can be achieved for ambient vapor phase and particle-phase mercury measurements using the methods described.

14.3.1.2 For particle-phase mercury, samples analyzed in duplicate can be used to assess analytical precision. Analytical precision for the methods described should average less than 10%.

14.3.1.3 For vapor phase mercury, samples can not be analyzed in duplicate. Repeated injections of vapor phase mercury standards can be used to assess the analytical precision which should average less than 5% for the methods described.

14.3.2 Accuracy

14.3.2.1 Accuracy can be assessed using standard reference materials (SRM) that have been analyzed in a manner identical to the field samples. However, SRMs do not currently exist for ambient vapor and particle phase mercury.

14.3.2.2 Comparison with other methods of analysis (i.e. neutron activation) or inter-laboratory comparisons can be used to assess accuracy.

15. References

1. Bloom, N.S. and 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.*, 208:151, 1988.
2. Burke, J., Hoyer, M., Keeler, G., Scherbatskoy, T., "Wet Deposition of Mercury and Ambient Mercury Concentrations at a Site in the Lake Champlain Basin," *Water, Air, and Soil Pollution*, 80:353-362, 1995.
3. Dumarey, R., Dams, R., and Hoste, J., "Comparison of the Collection and Desorption Efficiency of Activated Charcoal, Silver, and Gold for the Determination of Vapor phase Atmospheric Mercury," *Anal. Chem.*, 57:2638-2643, 1985.

4. Dumarey, R., Temmerman, E., Dams, R. and Hoste, J., "The Accuracy of the Vapor-Injection Calibration of Mercury by Amalgamation/Cold-Vapour Atomic Absorption Spectrometry," *Anal. Chim. Acta.*, 170:337-340, 1985.
5. Dvonch, J.T., Vette, A.F., Keeler, G.J., Evans, G., and Stevens, R., "An Intensive Multi-Site Pilot Study Investigating Atmospheric Mercury in Broward County, Florida," *Water, Air, and Soil Pollution*, 80:169-178, 1995.
6. Fitzgerald, W.F., and Gill, G.A., "Sub-Nanogram Determination of Mercury by Two-Stage Gold Amalgamation and Gas Phase Detection Applied to Atmospheric Analysis," *Anal. Chem.*, 15:1714, 1979.
7. Keeler, G., Glinsorn, G., and Pirrone, N. "Particulate Mercury in the Atmosphere: It's Significance, Transport, Transformation and Sources" *Water, Air, and Soil Pollution*, 80:159-168, 1995.
8. Lamborg, C., Hoyer, M., Keeler, G., Olmez, I., and Huang, X. "Particle-Phase Mercury in the Atmosphere: Collection/Analysis Method Development and Applications," in *Mercury as a Global Pollutant: Toward Integration and Synthesis*, Watras, C. and Huckabee, J. Eds., Lewis Publishers, 1994.
9. Bloom, N.S., "Determination of Picogram Levels of Methylmercury by Aqueous Phase Ethylation, Followed by Cryogenic Gas Chromatography with CFAS" *Can. J. Fish Aq. Sci.*, 46:1131, 1989.
10. Bloom N.S., Prestbo E.M., Hall B. and E.J. von der Geest, "Determination of Total Gaseous Hg in the Ambient Atmosphere by Collection on Iodated Carbon, Hot Acid Digestion and CFAS" *Water, Air and Soil Pollut.*, 80:1315, 1995.
11. Vermette S., Lindberg S., and N.S. Bloom, "Field Tests for a Regional mercury Deposition Network - Sampling Design and Preliminary Test Results," *Atmos. Environ.*, 29:11, 1995.
12. Prestbo E.M., Liang L., Horvat M., and N.S. Bloom, *Recent Advances in the Analytical Techniques for the Quantification of Mercury and Mercury Compounds in Different Media*, USEPA 600-R-92-105 (1992).

TABLE 1. EXAMPLE OF AMOUNT OF Hg INJECTED FOR A TYPICAL VAPOR PHASE CALIBRATION CURVE

Volume of Hg Saturated Air Injected (FL)	Amount of Hg Injected (ng)
0	0
20	0.198
40	0.396
80	0.793
160	1.586

Note: Flask temperature = 16.6EC
 Vapor density = 9.912 ng/cm³
 1 cm³ = 1,000 FL

TABLE 2. EXAMPLE OF AMOUNT OF Hg IN 5 mL ALIQUOT ANALYZED FOR A TYPICAL PARTICLE-PHASE CALIBRATION CURVE

Volume of 2 ng/mL Hg Standard Added (FL)	Amount of Hg in 5 mL Aliquot Analyzed (pg)
0	0
200	97
400	191
1,000	465
2,000	889

TABLE 3. EXAMPLE VAPOR PHASE Hg CALIBRATION CURVE

Hg Standard Concentration, pg Hg	Response, Peak Area Units (PAU)	Response-Zero Point, Peak Area Units (PAU)	Predicted Value, pg Hg	Percent Difference from Standard
0	41,193	0	0	
198	1,866,300	1,825,107	193	-3
396	3,729,482	3,688,289	390	-2
793	7,451,226	7,410,033	784	-1
1,586	15,083,592	15,042,399	1,592	0

$$\text{Slope} = 1.0585\text{E-}7 \text{ ng Hg/PAU}$$

$$r^2 = 0.9999$$

TABLE 4. EXAMPLE PARTICLE-PHASE Hg CALIBRATION CURVE

Hg Standard Concentration, pg Hg	Response, Peak Area Units (PAU)	Response-Zero Point, Peak Area Units (PAU)	Predicted Value, pg Hg	Percent Difference from Standard
0	168,320	0	0	0
97	1,144,900	976,580	89	-8
191	2,158,900	1,990,580	181	-5
465	5,204,200	5,035,880	459	-1
889	9,993,400	9,825,080	895	1

$$\text{Slope} = 9.1091\text{E-}5 \text{ pg Hg/PAU}$$

$$r^2 = 0.9995$$

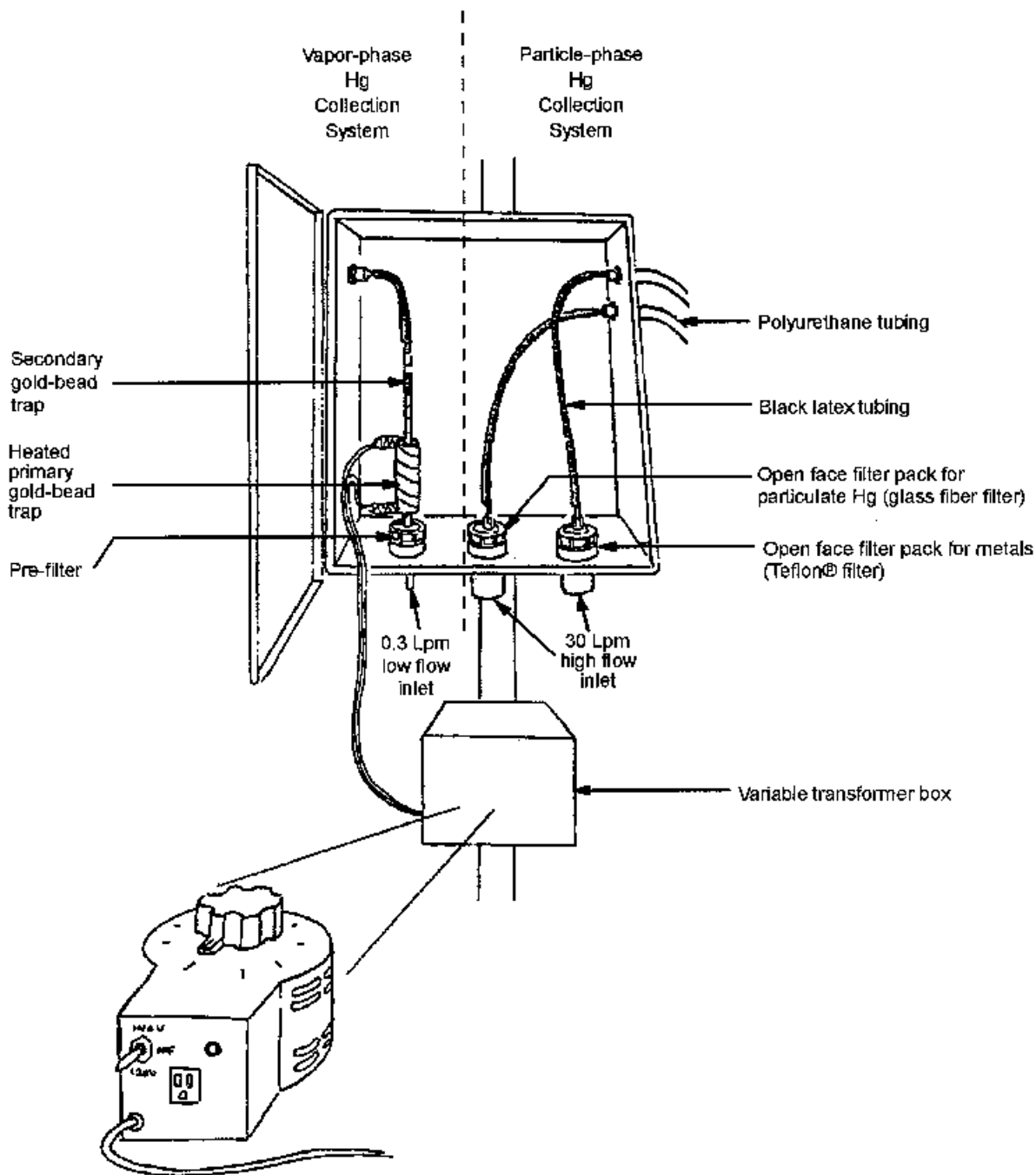


Figure 1. Example of ambient sampling system for collection of vapor and particle phase mercury.

**Sampling Vapor and Particle Phase
 Mercury in Ambient Air**

Project _____
 Site _____
 Location _____
 Date _____
 Height above ground _____
 Operator _____

Barometric Pressure (mmHg) _____
 Ambient Temperature (EC) _____
 Rain (Y/N) _____
 Relative Humidity (%) _____

Before	After

CARTRIDGE INFORMATION

Vapor-phase System

Primary gold-bead "A" trap I.D. Number _____
 Secondary gold-bead "B" trap I.D. Number _____
 Heated primary trap temperature (EC) _____

Particle-phase System

Filter pack I.D. Number _____

FIELD DATA INFORMATION

Clock Time (24-hr)	Flow Check (T)	Vapor-phase System		Particle-phase System		Total Sample Time, minute	Total Sample Volume, L
		Mass Flow Control Setting	Flow Rate (Q _a) (Lpm)	Dry Gas Reading	Flow Rate (Q _a) (Lpm)		

Comments _____

Figure 2. Field test data sheet (FTDS) for sampling vapor and particle phase mercury in ambient air.