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Method for Determination of Hg Concentration in Stack Gas Using Carbon Traps



Saint-Petersburg, Russian Federation

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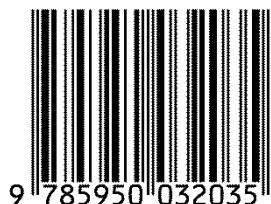
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**METHOD FOR
DETERMINATION OF
HG CONCENTRATION
IN STACK GAS USING
CARBON TRAPS**

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Date:

19 May 2017

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ACRONYMS AND ABBREVIATIONS

µg	microgram
µl	microliter
%	percent
°C	degrees Celsius
AAS	atomic absorption spectrometry
B	breakthrough, %
Bws	moisture content of sample gas as measured by US EPA Method 4, %/100.
ASTM	American Society of Testing Materials
C _a	concentration of mercury for the sample collection period, for sorbent trap “a”, µg/dscm
C _b	concentration of mercury for the sample collection period, for sorbent trap “b”, µg/dscm
CCVS	Continuing Calibration Verification Standard
C _d	mercury concentration, dry basis, µg/dscm
CO ₂	carbon dioxide
C _{rec}	concentration of spiked compound measured, µg/m ³
CRM	Certified Reference Material
C _w	Hg concentration, wet basis, µg/m ³
DGM	dry gas meter
dscm	dry standard cubic meter
dscm/min	dry standard cubic meter per minute
Hg	mercury
Hg ⁺²	oxidized mercury
Hg ⁰	elemental mercury
kPa	kilo Pascals
L	liter
LPM	liter per minute
m ₁	mass of mercury measured on sorbent trap section 1, µg
m ₂	mass of Hg measured on sorbent trap section 2, µg

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m ²	square meter
MDL	method detection limit
MFC	mass flow controller
mg	milligram
mm	millimeter
m _{recovered}	mass of spiked Hg recovered in Analytical Bias or Field Recovery Test, µg
m _s	total mass of Hg measured on the spiked trap in Field Recovery Test, µg
m/sec	meter per second
m _{spiked}	mass of Hg spiked in Analytical Bias or Field Recovery Test, µg
m _u	total mass of Hg measured on the unspiked trap in Field Recovery Test, µg
ng	nanogram
O ₂	oxygen
PM	particulate matter
QA	quality assurance
QC	quality control
R	recovery (of spiked mass, %)
RATA	Relative Accuracy Test Audits
RD	relative deviation (between the mercury concentrations from traps “a” and “b”, %)
TC	thermocouple
the Convention	Minamata Convention on Mercury
US	United States
US EPA	United States Environmental Protection Agency
V _s	volume of gas sampled, spiked trap in Field Recovery Test, dscm
V _t	total volume of dry gas metered during the collection period, dscm; for the purposes of this method, standard temperature and pressure are defined as 20° C and 101.3 kPa (760 mm Hg), respectively [cf. Equation (7)]
V _u	volume of gas sampled, non-spiked trap in Field Recovery Test, dscm

1 INTRODUCTION

Mercury (Hg) is a known neurotoxin. Most exposure to Hg occurs through ingestion of fish contaminated with organic (methyl) Hg. Inhalation of elemental Hg vapors is also a relatively common form of exposure. Hg is released into the atmosphere from various industrial processes such as coal combustion, cement production, waste incineration, and non-ferrous metals smelting. Coal contains trace amounts of mercury, which are released into the atmosphere in various forms by combustion. Because of large amounts of coal combusted around the world, coal combustion is the second largest source of mercury emissions from anthropogenic sources globally. These various forms of Hg emitted into the atmosphere eventually undergo the process of bioaccumulation, conversion to organic Hg, and end up in (predominantly) larger fish.

To address Hg-related issues globally, the United Nations Environmental Programme has developed the Minamata Convention on Mercury (the Convention). Article 8 of the Convention addresses controlling and, where feasible, reducing emissions of mercury and mercury compounds to the atmosphere from the point sources in categories listed in Annex D to the Convention. The list of point source categories in Annex D includes coal-fired power plants, coal-fired industrial boilers, non-ferrous metals smelting and roasting processes, waste incineration plants, and cement clinker production plants.

Because of the toxicity of Hg, it is important to know the amount of Hg emissions released by point sources. Several methods are available to measure Hg emissions. These methods differ in level of complexity, application conditions, and their ability to speciate Hg (ability to differentiate the elemental form of Hg from oxidized form of Hg). The most commonly used Hg measurement methods include the following: United States (US) Environmental Protection Agency (US EPA) Method 30B, US EPA Method 29, and the Ontario Hydro Method (American Society of Testing Materials [ASTM] D6784). US EPA Method 30B - Determination of Total Vapor Phase Mercury Emissions from Coal-Fired Combustion Sources Using Carbon Sorbent Traps - will be discussed in the following section.

The scope of this document is description of the procedure for the determination of vapor phase Hg mass concentration in stack gas using carbon traps based on US EPA Method 30B. The procedure can be applied in countries around the world. Exact requirements for the performance of US EPA Method 30B can be downloaded in electronic form from <https://www3.epa.gov/ttn/emc/promgate.html>. Careful consideration should be exercised to reconcile the requirements of US EPA Method 30B and local requirements in countries around the world. The US EPA has developed so called "US EPA's Mercury Measurement Toolkit" (The Toolkit) which enables rapid and cost-effective measurements of Hg (including its speciation) in stack gases, coal, fly ash, and other matrices. The Toolkit has been used for United Nations Environmental Programme-sponsored projects to conduct on-site testing to determine the mercury content in stack gases.

This document consists of two parts, together describing necessary procedures for the determination of vapor phase Hg mass concentration in stack gas using carbon traps. Determination of mass concentration of total vapor phase Hg includes elemental Hg (Hg⁰) and oxidized Hg (Hg⁺²). Part I addresses the exposure of carbon traps to stack gas. Part II

addresses the analysis of carbon traps that have been exposed to stack gas according to procedures described in Part I. PART II of this document specifies Hg analysis of carbon traps by thermal desorption/direct combustion Hg recovery followed by atomic absorption spectrometry (AAS) analysis. Other recovery techniques may include acid leaching, digestion, or thermal desorption/direct combustion. Other analytical techniques may include atomic fluorescence spectrometry and X-ray fluorescence. Carbon traps exposed to stack gas may be transmitted to a laboratory for the analysis. In some instances, the analysis of carbon traps exposed to stack gas may be conducted by the sampling crew at the sampling site.

2 BRIEF DESCRIPTION OF US EPA METHOD 30B

US EPA Method 30B - Determination of Total Vapor Phase Mercury Emissions from Coal-Fired Combustion Sources Using Carbon Sorbent Traps is intended to quantify vapor phase Hg emissions, including Hg⁰ and Hg⁺² from coal-fired power plants. The US EPA Method 30B is not an isokinetic method and thus can only be used in cases where very low particulate matter (PM) concentration is present (e.g., when conducting sampling after all operating PM control devices).

If low PM conditions are not present, sampling at multiple points in the stack may be required or another Hg measurement method such as US EPA Method 29 should be used. US EPA Method 29 uses isokinetic procedures that can account for higher PM concentrations. However, this method yields total mercury only and cannot differentiate between Hg⁰ and Hg⁺². The Ontario Hydro method (ASTM D6784) can quantify PM-bound Hg, Hg⁰, Hg⁺², and total Hg in coal-fired power plant stacks with modest PM concentrations.

In US EPA Method 30B, the flue gas sample is vacuum extracted using a heated sample probe and calibrated dry gas meter (DGM)/pump system shown in the sampling train schematic in Figure I-1. Hg is captured by absorption onto paired, in-stack carbon tube traps (two traps exposed to stack gas in parallel). These traps can later be analyzed using any instrument or technology capable of quantifying Hg from the sorbent media and meeting the performance criteria spelled out in the method. Many analytical methods for Hg utilize thermal desorption and AAS in some form. Other wet and dry separation techniques and analytical procedures are allowed which can meet the performance criteria. Detailed procedures for a variety of potential analytical approaches can be seen at <http://www.epa.gov/ttn/emc>.

US EPA Method 30B was developed primarily for use as a reference method for relative accuracy test audits (RATAs) of vapor phase Hg continuous emission monitoring systems and sorbent trap monitoring systems installed at coal-fired boilers. However, it is also appropriate for Hg emissions testing at such boilers. Notably, when used alone, USEPA Method 30B only determines Hg concentration in stack gas. To determine the mass emission rate of Hg, other stack parameters must be known. These parameters can be determined by the concurrent performance of:

- US EPA Method 1 – Sample and Velocity Traverses for Stationary Sources (determines sampling traverse points in the stack);
- US EPA Method 2 – Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube);

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- US EPA Method 3 – Gas Analysis for the Determination of Dry Molecular Weight; and
- US EPA Method 4 – Determination of Moisture Content in Stack Gas. These methods, along with Method 30B, can be found in print form in 40 Code of Federal Regulations Part 60.

The above methods can be downloaded in electronic form:

<https://www3.epa.gov/ttn/emc/promgate.html>.

During each US EPA Method 30B sampling run, paired sorbent traps (sorbent traps exposed to stack gas in parallel), consisting of one sorbent trap for speciated Hg determination and one total Hg sorbent trap spiked with a known amount of Hg⁰ are used. With this arrangement, the determination of measurement precision and a sorbent trap recovery test are made possible. Generally, three good sampling runs constitute a valid stack test for Hg.

PART I EXPOSURE OF CARBON TRAPS TO STACK GAS

I.1 DEFINITIONS USED IN THIS PROCEDURE

Sampling Train: The entire mercury sampling system including sorbent tube traps, sampling probe, heated sample line and filter, moisture removal system, unheated sample lines, and sampling console.

Sorbent Trap for total Hg determination: A cartridge or sleeve containing a sorbent media (typically glass tube with activated carbon treated with iodine or some other halogen) with two sections separated by an inert material such as glass wool. In the direction of gas flow, the first section provides the primary capture of Hg. The second section serves as a backup section for determination of Hg breakthrough. Glass wool is placed at the inlet of the tube, between sections, and at the outlet of the tube. Hg captured in the wool is included in the total Hg measured and will include PM-bound Hg.

Sorbent Trap for speciated Hg determination: A cartridge or sleeve containing a sorbent media (typically glass tube with activated carbon treated with iodine or some other halogen) with multiple sections separated by an inert material such as glass wool. In the direction of gas flow, the first section captures acid gases. The next two sections, sections 2 and 3, are filled with potassium chloride and provide the primary capture of Hg^{+2} and a backup section for determination of Hg^{+2} breakthrough, respectively. The following sections, sections 4 and 5, are filled with iodated activated carbon and provide the primary capture of Hg^0 and a backup section for determination of Hg^0 breakthrough. In this way these sorbent traps are optimized for the quantitative capture of elemental and oxidized forms of Hg and can be analyzed by multiple techniques. Glass wool is placed at the inlet of the tube, between sections, and at the outlet of the tube. Hg captured in the wool is included in the total Hg measured and will include PM-bound Hg.

Sample probe: Heated stainless steel tube containing sample lines, thermocouples (TCs) and heater controls.

Heated sample line: Heated tubing between the sampling probe and the moisture removal system conveying the sample gas and containing TCs and heater controls.

Moisture removal train: Series of moisture removal impactors and desiccants used to protect the dry gas meter and pump.

Sampling Console: Unit consisting of meter box with valves, sample pump, DGM, TCs, TC readout, and heater controls.

Test: Series of runs required by the applicable regulation in the country/location where sampling is performed.

Thermal Analysis: Analytical technique where the contents of the sorbent tube trap previously exposed to flue gas are analyzed using a thermal technique to release the Hg captured by the sorbent tube trap in a detectable form for quantification.

Wet Analysis: Analytical technique where the contents of the sorbent tube trap previously exposed to flue gas are chemically treated to quantitatively transfer the Hg captured by the sorbent tube trap to liquid solution for subsequent analysis.

I.2 EQUIPMENT AND SUPPLIES

The equipment and supplies necessary to successfully perform US EPA Method 30B are listed and discussed in this section. The necessary equipment and supplies for sampling train components are listed in Table I-1 below in order from the probe to the sampling console, as shown in Figure I-1. Section I.5 discusses preparation and necessary calibration procedures for these supplies and equipment. The sampling train components are discussed in more detail in Section I.6. It should be noted that mention of any specific manufacturer or appearance of trade names in figures does not construe endorsement of any products. Equivalent equipment from other manufacturers could be used for the performance of this procedure based on US EPA Method 30B.

Figure I-1: US EPA Method 30B sampling train schematic

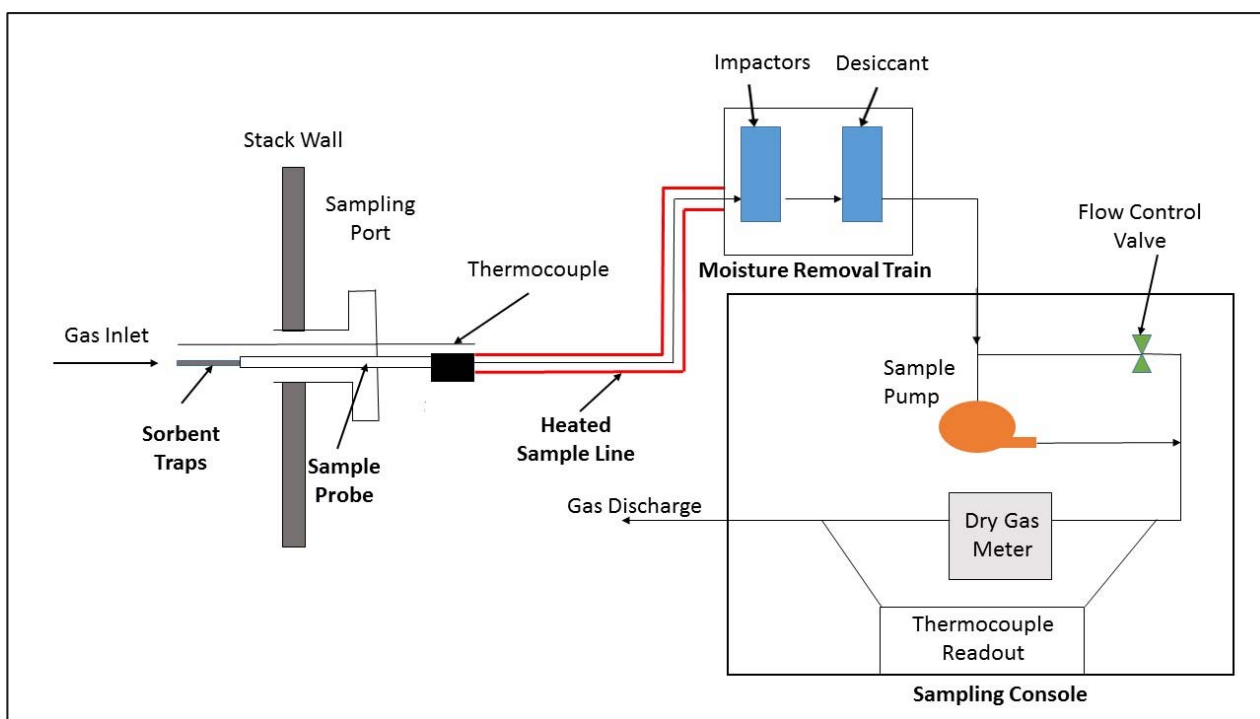


Table I-1 lists the major items making up a US EPA Method 30B sampling train as well as ancillary and support equipment necessary for successful sampling. Further details are discussed below.

The major part of sampling equipment is the sample probe shown in Figure I-2. The probe is constructed of stainless steel and contains connections for the carbon tube traps, stack gas sample lines, particulate filter heater box, filters, a heating element to prevent moisture condensation, K-type TCs (stack temperature and probe temperature) and a strain relief mount for the heated umbilical cord. The probe shown in Figure I-2 has connections for four tube traps; some probes may have connections for only two tube traps. The heated box shown on the far end (the end of the probe opposite to the one with yellow caps) of Figure I-2 holds the PM filters.

The heated sample line (orange line at the end of the sample probe) can also be seen in Figure I-2. This is heavy so precautions must be taken when mounting it to the probe as it can cause

the probe to become imbalanced and sag or fall. The heated sample line conveys sample flow to the moisture removal train. It is heated and can become very hot. Use of heavy gloves when handling is recommended.

The portable sampling system shown in Figure I-2 consists of a sampling console, a pair of desiccant driers, a sampling probe, blower and connection hose, air lines, power lines, and a thermocouple line.

The sampling console shown in Figure I-3 is a dual train sampling system with mass flow controllers (MFCs), vacuum pressure gauges, and heater with thermocouple input and probe power port. MFCs can set independent flow rates for both trains. The sampling probe can be either heated or cooled by a separate blower. At the base of the probe, there are two independent thermocouple connectors.

Table I-1: US EPA Method 30B Sampling and Ancillary/Support Equipment

Item	Purpose
Sorbent Traps	Capture Hg in-stack by absorption.
Sample Probe	Holds carbon tube traps and conveys sample gas to the rest of the sampling train; it also contains stack and probe temperature sensors (K-type TCs) and filters for particulate removal in an attached heated box.
Heated Sample Line	Conveys wet sample gas from sample probe to moisture removal train; it also contains TC lines from the stack temperature sensor, heated umbilical temperature sensor and probe temperature sensor (K-type TCs) to a temperature indicator in meter box as well as the electrical wires for probe, filter box and umbilical heating.
37-millimeter Quartz Filter Media	Provides PM removal
Moisture Removal Train	Removes moisture in the stack gas to protect the dry gas meter.
Unheated Sample Lines	Convey dry sample gas from the moisture removal train to the meter box; they also connect individual moisture removal train components.
Flow Rate Meter and Control Valve	Adjusts and gives a real-time indication of the stack gas volumetric flow rates.
Temperature Readout for Stack, Probe, Dry Gas Meter, Moisture Removal Train and Heated Line	Indicates temperatures for use in sample train control and emissions calculations.

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Item	Purpose
Vacuum Pump	Provides vacuum to convey the sample gas through sampling train.
Dry Gas Meter (DGM)	Accurately quantifies sample gas volumes.
Elapsed Timer	Times the sampling run.
Alumisorb Desiccant	Goes in canisters in the moisture removal train; dries stack gas to protect dry gas meter.
Plastic Tube Trap End Caps	Attach to end of tube traps for leak checks of sampling train and to protect tubes from contamination during handling and shipping.
Barometer	Used to correct sample volume to standard conditions.
Plastic Tubing, 10-millimeter (mm)	DGM flow accuracy checks.
Certified Gas Flow Meter, (0.5-5.0 liters per minute [LPM])	DGM flow accuracy checks.
Stopwatch	DGM flow accuracy checks.
Mercury thermometer	TC accuracy checks.
Duct Tape	General use
Tarps	Rain covers
Rain Gear	Rain protection
Heavy Gloves	Burn protection
Box End Wrenches, 9-16 mm	Tube trap mounting
Rope or Chain	Sampling probe support
Protective Wrap	Tube trap packing for laboratory
Sealable Plastic Bags	Laboratory chain of custody form packaging
Logbook	Recording of flow check data and process conditions
Laboratory Chain of Custody Forms	Sorbent tube trap documentation for laboratory
Sampling Data Sheets	Recording of sampling run data

Figure I-2: Sample probe



Figure I-3: Dual sampling console and sample probe



I.3 EQUIPMENT PREPARATION AND CALIBRATION

All equipment must be prepared for use, assembled, and leak checked prior to the commencement of Hg sampling. Accuracy checks of the DGMs and TCs must also be performed prior to sampling. In addition, the DGMs and TCs must have been previously calibrated and documented in a laboratory setting. Equipment calibration on the stack is not practical.

I.4 SAMPLING TRAIN ASSEMBLY AND PRE-TEST LEAK CHECK

After the arrival of the sampling crew at the site, components of the sampling train need to be carefully assembled. The following describes the sequential steps of the procedure for the sampling train assembly.

1. Transport the individual sampling train components to the sampling location.
 - a. Inspect the sampling port(s) to determine the best way to support the sampling probe.
 - b. Confirm the sampling ports are not clogged. It is also recommended cleaning the inside of the ports so no loose PM can cause a stoppage of sample flow into the tube traps.
 - c. Supporting the sample probe may require the erection of a legged-tray or chain/rope support system to safely immobilize the sampling probe during the sampling runs. Ensure the support system is sturdy enough to support the

weight of the heated umbilical cord attached to the probe and it will not be damaged by the hot probe.

2. Open the heated filter box and separate the filter holder halves.
 - a. Install fresh 37-mm quartz filter and reassemble.
 - b. Attach the heated sample line to the sample probe by affixing the stainless-steel relief clamps (see Figure I-4).
 - c. Then use wrenches to complete the attachment of the sample lines to the filter holder exits with swaged tube fittings. This must be done very carefully as it is easy to confuse the two sample lines – it is recommended they be color coded (for example, by wrapping them with colored tape) to aid in accurate identification.
 - d. Attach the K-type TC lines (for the stack, filter box and probe temperature) and attach electrical power line for the probe and filter box heaters.
3. Attach the sample lines on the opposite end of the heated sample line to the moisture removal train. Attach the unheated sample lines from the moisture removal train to the meter box. Color-coding is recommended for both tasks.
4. Attach the yellow K-type TC lines from the heated sample line and moisture removal train to the meter box. The K-type TC lines are clearly labeled.
 - a. Attach the heated sample line power cord to the meter box and then attach the meter box power cord to the meter box.
 - b. Plug the meter box power cord into an electrical outlet.
5. Turn the meter box main power on and set the probe and heated umbilical temperatures to 180 degrees Celsius (°C) and allow them to stabilize before sampling. Do not touch the probe or heated sample line cord without heavy gloves, as they will be extremely hot.
 - a. Turn on both sampling pumps for warm-up; do not open the flow valves. This will insure the electrical supply is sufficient to handle maximum power use for the sampling train.
 - b. After warming the pumps up for approximately 10 minutes, set the flow on both sample channels to 1.0 LPM using the course and fine sample flow valves and the rotameters.
 - c. Turn the sample pumps off.

After successful assembly, the sampling train must be leak-tested before the actual test can take place. To perform a pre-test sampling train leak check, complete the following steps.

1. Attach the carbon tube traps to the Teflon swage nuts on the end of the sample probe; tighten the swage nuts snugly but carefully. There may be more than one type of tube traps, (e.g., one for total vapor phase Hg and one for speciated Hg). This will be clear from the labeling attached to the tube traps by the laboratory.

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- a. Make sure all pertinent information is recorded on the data sheet and/or the logbook.
2. Affix tube trap end caps snugly to the end of the mercury tube traps.
3. Turn both sample pumps on and watch the rotameters. The flow ball should drop to the bottom of the rotameters tube with no movement whatsoever. If it does not, a leak is occurring in the system.
 - a. Troubleshoot by checking plumbing connections and look for broken or damaged parts or components until the leak is identified; it will usually be at one of the swage fittings or a broken/pierced sample line.
4. If no leak is found, turn the sampling pumps off with their switches and remove the plastic end caps from the tube traps to allow the vacuum to equilibrate.
 - a. Turn the course sample flow valves to the closed position and replace the plastic end caps on the tube traps. The sampling train is now ready for mercury sampling.

Following the successful pre-test leak test, the sampling train is ready for calibration.

Figure I-4: Heated sample line strain relief attachment to heated filter box



Figure I-5: Sample probe with end caps installed



I.5 EQUIPMENT CALIBRATION

Detailed procedures for the accomplishment of multi-point equipment calibrations can be seen in US EPA Method 2 for TCs and US EPA Method 5 for DGMs. They include calibration of the DGMs and TCs with National Institute of Standards and Technology (US) standard devices. Calibration intervals are dictated by local regulatory requirements. Accuracy checks of the DGMs and TCs prior to use in the field are recommended and will prevent the use of inaccurate equipment that will compromise test integrity. These checks should be performed in the laboratory prior to taking the equipment to the stack.

An on-site calibration check of a DGM can be performed with a certified gas flow meter of the proper flow range (0.5-5 LPM).

To perform the check, install a sorbent tube trap (an old or contaminated sorbent tube trap is usually designated as a flow check trap and labeled "FC") on the probe tip for the flow channel to be checked.

- a. Perform a leak check as detailed in Section I.4. If it unsuccessful, perform the troubleshooting procedure described in the same section.
- b. If successful, connect a length of plastic tubing between the tip of the flow check tube trap and the exit of the gas flow meter.
- c. Make sure the course sample flow valve is off.
- d. Turn the gas flow meter and the sample pump on and allow them to warm up for 10 minutes.
- e. When the warm-up period is complete, record the DGM reading in a logbook.
- f. Then, simultaneously, start the stopwatch and set a sample flow rate of 1.0 LPM on the rotameters of the channel to be flow checked.
- g. Note the reading of the rotameters and the gas flow meter in the logbook. Monitor for 10-minutes while making no adjustment to the sample flow rate.
- h. Record the rotameter reading and the gas flow meter reading at one-minute intervals during the 10-minute flow check.
- i. At the end of the 10-minute period, turn off the sample pump with the switch or quickly turn the course sample flow valve to the off position.
- j. Record the DGM reading in the logbook.
- k. The difference between the final and initial DGM readings, divided by the 10-minute flow check elapsed time, is the calculated DGM sample flow rate in LPM. This figure should agree with the average of the 1-minute certified gas flow meter readings within ± 5 percent (%).
- l. If it does not, the DGM cannot be used for testing and must be re-calibrated.
- m. As an additional check, compare the calculated DGM sample flow rate with the average rotameter reading. These values should be in good agreement ($\pm 10\%$) but are not critical.

- n. If the rotameter reading is significantly off, troubleshoot for leaks at its inlet and exit fittings.

A field accuracy check of the TCs must also be performed. Two different procedures are used, depending on ease of access to the TC tips. With the stack temperature TC, easy access allows a three-point temperature accuracy check procedure. This temperature is a critical parameter and cannot be ignored.

Step-wise calibration procedure is given below.

- a. A current calibration certification document must be on hand.
- b. Make sure the sample probe tip and the mercury thermometer are shaded from the sun and the sample probe heat, filter box heat and heated sample line heat are off and stabilized.
- c. In the logbook, record ambient temperature as indicated by the mercury thermometer and stack temperature as indicated by the TC readout on the meter box.
- d. Next, immerse the Hg thermometer and the sample probe tip in an ice water bath (a small bucket should suffice for this purpose). Wait until the temperatures indicated by the mercury thermometer and stack temperature as indicated by the TC readout on the meter box stabilize (~ 1 minute) and record them in the logbook.
- e. Remove the Hg thermometer and the sample probe tip from the ice bath and immerse in a boiling water bath. Wait until the temperatures indicated by the Hg thermometer and stack temperature as indicated by the TC readout on the meter box stabilize (~ 1 minute) and record them in the logbook.
- f. Remove the Hg thermometer and the sample probe tip from the boiling water bath and allow them to stabilize in ambient air (shaded) for 10 minutes.
- g. In the logbook, record ambient temperature as indicated by the Hg thermometer and stack temperature as indicated by the TC readout on the meter box.
- h. No individual stack temperature as indicated by the TC readout on the meter box should differ from its corresponding mercury thermometer reading by more than 1 °C. A greater difference requires a calibration check of the TC in question prior to use in mercury sampling.

An identical procedure to that described above can be used for the heated filter box TC if it can be removed from its placement in the box and immersed. If not, the two-point procedure described below can be used. For the moisture removal train TC, the same procedure can also be used if it can be accessed for immersion, with the exception that the boiling water step is unnecessary; it never sees temperatures this high. In any case, these TCs do not monitor critical parameters and can be safely ignored if they read accurate ambient temperature vs the mercury thermometer when off and shaded.

A two-point temperature field accuracy check procedure must be used for the DGM TCs. These are critical parameters and must not be ignored; the calibration certification must be current.

- a. Open the meter box and tape the Hg thermometer to the DGM being checked; place it as close as possible to the TC probe fitting on the DGM.
- b. Close the meter box (leaving a small crack to view the Hg thermometer) and place it in the shade.
- c. Turn the main power of the meter box on; this should activate the cooling fan. With all heaters and pumps off, allow the temperature in the meter box to stabilize for 10 minutes and record the Hg thermometer temperature and the DGM temperature as indicated by the TC readout on the meter box.
- d. Next, move the meter box into the sun and switch on the two sample pumps. The meter box temperature will immediately begin to rise. Wait until it stabilizes and record the Hg thermometer temperature and the DGM temperature as indicated by the TC readout on the meter box.
- e. The temperature spread between the two temperatures (shaded and un-shaded with pumps on) should be large enough to cover a large portion of the temperature regime the meter box will see in use. The Hg thermometer temperature and the DGM temperature as indicated by the TC readout on the meter box should agree within $\pm 1^{\circ}\text{C}$. This is critical parameter and any difference greater than that should trigger a calibration check of the TC in question prior to use in Hg sampling.
- f. The TC for the heated sample line is difficult to check because it is embedded in a thick sheath. One possible way to check it is to tape the Hg thermometer to the surface of the sheath and cover it with a towel while shaded. Then compare that temperature with the heated sample line temperature as indicated by the TC readout on the meter box while the heater is on and stabilized. The temperature of the heated sample line is not a critical parameter but is important to keep moisture condensation from dripping back into the Hg tube traps when the sampling probe is mounted in the stack vertically.

Following successful leak test and pre-test calibration, the sampling train is ready for Hg sampling. The Hg sampling procedure is discussed in the following Section I.6.

I.6 SAMPLING PROCEDURE

After a successful pre-test leak check (results must be recorded on the Sampling Data Sheet) and on-site DGM calibration, Hg sampling can commence. Carefully record the tube trap numbers, DGM IDs, and sampling probe location for each sorbent tube trap on the data sheet provided with the tube traps and on the Sampling Data Sheet (shown in Appendix A). Also make note of process conditions (operating load, control device parameters, etc.) in the logbook and/or on the margins of the Sampling Data Sheet; continue to make logbook such notes during the sampling run if any of these parameters change.

Detailed, stepwise instructions for operating the sampling train are given below.

1. Remove the plastic end caps from the tube traps.
2. Remove the port cap and insert the sample probe into the stack; securely support the sample probe with chain or rope. This insertion must be done very carefully as the glass tube traps are easily broken. Use heavy gloves as the sample probe will be extremely hot.
3. Seal the annulus around the sample probe.
4. Record the required preliminary information on the Sampling Data Sheet.
5. Turn the main meter box power on. Reset the DGM totalizers to 0.000 and the run elapsed timer to zero.
6. Open both course sample flow rate valves and start the run elapsed timer. Adjust the fine sample flow rate valves to 1.0 LPM on the rotameters on both flow channels.
7. Record the run start time (local time) on the Sampling Data Sheet. Record the sample flow rates shown on the rotameter and the DGM temperatures as indicated by the TC readout on the Sampling Data Sheet; the latter will require switching the TC readout input between the two flow channels with the selector switch above the TC line input fittings.
8. Repeat recording of the sample flow rates shown on the rotameter and the DGM temperatures as indicated by the TC readout every five minutes for the duration of the sampling run.
9. Repeat adjustment of the sample flow rate valves on both flow channels as necessary to maintain both sample flow rates at 1.0 LPM on the rotameters throughout the sampling run.
10. When the desired sample run time has been reached, turn off the course sample flow valves and turn off the run elapsed timers.
11. Record the final sample volumes as indicated on the two DGM totalizers and record the run end time (local time) on the Sampling Data Sheet.
12. Carefully remove the sample probe from the stack (to avoid breakage of the tube traps) with heavy gloves and set it on a handrail or table where it can be firmly supported. Replace the port cap.

13. Wait until the tube traps are cool (they and the sampling probe will be extremely hot when first extracted from the stack) and perform a leak check as detailed in Section 5.1; record it on the Sampling Data Sheet.
14. Perform a post-test calibration check as detailed in Section I.4. If it is not successful, the sampling run must be repeated after a re-calibration of the sampling pump or with a different sampling train. If the post-test calibration check is successful, remove the calibration check equipment and proceed to step 15.
15. Remove the tube traps from the sampling probe with wrenches and cap both ends with plastic end caps. Place the tube traps in the packaging they came in, carefully replacing the tissue used to protect the tubes, and send them in a small box, along with the Sampling Data Sheets down to the staging area for data reduction and shipment to the laboratory.
16. Prepare the sampling train for the next sampling run by following the procedures in Section I.4.
17. On the ground, fill out the laboratory chain of custody form (an example shown in Appendix B). This form must be completed in full as the laboratory will need all information to be able to proceed with sample analyses.
18. Pack the tube traps into an appropriately sized cooler with dry ice for shipment to the laboratory. Use protective (bubble) wrap to protect them.
19. Make a copy of the laboratory chain of custody form and include the original with the samples enclosed in a plastic sealable bag.

Figure I-6: Sample probe insertion into stack



I.7 QUALITY ASSURANCE/QUALITY CONTROL

Table I-2 shows US EPA Method 30B quality assurance (QA) / quality control (QC) criteria related to field sampling using sorbent trap tubes.

Table I-2: Quality Assurance/Quality Control Criteria for Field Sampling

QA/QC Test or Specification	Acceptance Criteria	Frequency	Consequences if Not Met
Gas flow meter calibration (At 3 settings or points)	Calibration factor (γ_i) at each flow rate must be within $\pm 2\%$ of the average value (γ)	Prior to initial use and when post-test check is not within $\pm 5\%$ of γ	Recalibrate at 3 points until the acceptance criteria are met
Gas flow meter post-test calibration check (Single-point)	Calibration factor (γ_i) must be within $\pm 5\%$ of the γ value from the most recent 3-point calibration	After each field test. For mass flow meters, must be done on-site, using stack gas	Recalibrate gas flow meter at 3 points to determine a new value of γ . For mass flow meters, must be done on-site, using stack gas. Apply the new γ value to the field test data
Temperature sensor calibration	Absolute temperature measured by sensor within $\pm 1.5\%$ of a reference sensor	Prior to initial use and before each test thereafter	Recalibrate; sensor may not be used until specification is met
Barometer calibration	Absolute pressure measured by instrument within ± 10 mm Hg of reading with a mercury barometer	Prior to initial use and before each test thereafter	Recalibrate; instrument may not be used until specification is met
Pre-test leak check	$< 4\%$ of target sampling rate	Prior to sampling	Sampling will not commence until the leak check is passed

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QA/QC Test or Specification	Acceptance Criteria	Frequency	Consequences if Not Met
Post-test leak check	<4% of average sampling rate	After sampling	Sample invalidated*
Test run total sample volume	Within $\pm 20\%$ of total volume sampled during field recovery test	Each individual sample	Sample invalidated
Field recovery test	Average recovery between 85% and 115% for Hg ⁰	Once per field test	Field sample runs not validated without successful field recovery test

*Data from the pair of sorbent traps are also invalidated.

Adopted from: Method 30B Talking Points-Ohio Lumex

I.8 DATA COLLECTION AND CALCULATIONS

A Sampling Data Sheet for recording US EPA Method 30B Hg sampling data is shown in Appendix A. The Sampling Data Sheet needs to be completed in detail during all sampling runs. The data contained in the Sheet are critical to producing an accurate test report of the sampling results.

At the conclusion of each sampling run, calculate the sample volume in liters (L) by difference between final and initial DGM readings and record it at the bottom of the Sampling Data Sheet. Calculate an average of the remaining parameters on the Sampling Data Sheet and record them at the bottom. The laboratory may require these data. Sampling Data Sheet must be sent to the laboratory in the same package as sorbent trap tubes.

Upon receipt of the laboratory report, make note of the mass of Hg reported for each sampling run in micrograms (μg). Note that this quantity is a sum of the mass collected in the two sorbent sections of the tube traps (primary and breakthrough); this may not be pre-totaled in the laboratory report. To calculate the concentration of Hg in the stack gas, in $\mu\text{g}/\text{dry}$ standard cubic meter (dscm), for each sampling run, use the Equation (1) below:

$$[\text{Hg}] = \frac{M}{(V/1000) \cdot ((T + 273)/293) \cdot (29.92/P_b)} \quad (1)$$

Where:

[Hg]= concentration of Hg in the stack gas; $\mu\text{g}/\text{dscm}$

M= total mass of Hg reported by the laboratory (ensure that Hg mass for primary section and Hg mass for breakthrough section are added; μg)

V= sample volume; liters

T= average dry gas meter temperature recorded during Hg test; $^{\circ}\text{C}$

P_b = barometric pressure recorded during Hg test; inches of Hg; to convert kiloPascals (kPa) to inches of Hg, multiply the number of kPa by 0.295301).

Calculation of mass emission rates of Hg requires inputs from several other sampling methods:

- velocity and volumetric flow rate of stack gas from US EPA Methods 1 and 2
- oxygen (O_2) and carbon dioxide (CO_2) concentration of stack gas from US EPA Method 3 or 3A; and
- moisture content of stack gas from US EPA Method 4.

US EPA Method 1 shows how to choose velocity traverse points in the stack. US EPA Method 3 (or 3A) and US EPA Method 4 results are inputs into US EPA Method 2 to allow calculation of volumetric flow rate on a dry standard basis. US EPA Methods 1-4 procedures result in a volumetric flow rate expressed in dry standard cubic meters per minute (dscm/min). Specific calculations of stack gas velocity, V_s , in meter per second (m/sec) from US EPA Method 2 are

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presented in Equation (2) below and for volumetric flow rate, Q_s , in dscm/min from US EPA Method 2 are presented in Equation (6) below.

$$V_s = K_p \cdot C_p \cdot [\text{avg sqrt } \Delta p] \cdot \text{sqrt} [T_s/P_s \times M_s] \quad (2)$$

Where:

V_s = stack gas velocity; m/sec

K_p = 34.97 (equation unit constant)

C_p = 0.84 (S-type pitot constant)

Δp = velocity head readings from US EPA Method 2 data sheet; mm H₂O

T_s = average stack temperature from US EPA Method 2 data sheet; °C

P_s = stack pressure from US EPA Method 2 data sheet; inches Hg

M_s = molecular weight of stack gas, wet basis

sqrt = square root

avg sqrt = average sqrt

Equation (3) below must be used to calculate stack gas molecular weight on a wet basis, M_s , from US EPA Method 3.

$$M_s = M_d \cdot (1 - B_{ws}) + 18.0 \cdot B_{ws} \quad (3)$$

Where:

B_{ws} = moisture content of stack gas (%v/v) from US EPA Method 4

M_d = stack gas molecular weight on dry basis

Stack gas dry molecular weight, M_d , must be calculated from US EPA Method 3 data using Equation (4) below.

$$M_s = 0.44 \cdot (\%CO_2) + 0.32 \cdot (\%O_2) + 0.28 \cdot (\%N_2 + \%CO) \quad (4)$$

Where:

$\%CO_2$ = concentration of CO₂ in stack gas; v/v

$\%O_2$ = concentration of O₂ in stack gas; v/v

$\%N_2$ = concentration of N₂ in the stack gas; v/v

$\%CO$ = concentration of CO in the stack gas; v/v

Note that US EPA Method 3 does not yield results for $\%N_2$ and $\%CO$ in Equation (4). The value of $\%CO$ is generally assumed to be zero unless it is known to be higher and $\%N_2$ is calculated from US EPA Method 3 data using equation (5) below.

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$$M_s = 100 - (\%CO_2 + \%O_2). \quad (5)$$

Finally, standard stack gas volumetric flow rate, Q_s , is calculated using Equation (6) below.

$$Q_s = 3600 \cdot (1 - B_{ws}) \cdot V_s \cdot A_s \cdot \frac{293 \cdot P_s}{T_s \cdot 29.92}. \quad (6)$$

Where:

A_s = cross sectional area of stack (in m^2) from US EPA Method 1 data sheet.

Once the standard stack gas volumetric flow rate has been calculated using Equation (6) and using the Hg concentration results from US EPA Method 30B, [Hg] value from Equation (1), mass emission rate, E_{Hg} , can be calculated from Equation (7) below:

$$E_{Hg} = [Hg] / Q_s. \quad (7)$$

Where:

E_{Hg} = mass Hg emission rate; $\mu g/hr$.

1.9 SAFETY CONSIDERATIONS FOR STACK SAMPLING

Prior to field sampling for Hg as described in this procedure, an inspection of the sampling site should be made with the objective of identifying potential health and safety hazards. As the sampling location will likely be elevated above local grade, it should be determined if hand and guardrails are installed at appropriate locations. Safe supports for the sampling train should be installed. Sampling port caps should be loosened by facility maintenance personnel to avoid the danger of back strain by sampling personnel. Obstructions at or below head height should be removed, isolated or tagged with streamers to prevent a loss of balance when encountering them by sampling personnel.

Health and safety considerations during sampling should include high temperatures possibly encountered by the sampling crew as well as proper handling of heavy equipment. Ports and sample probes will be very hot and will require heavy gloves and caution when handling. Safety glasses and acid gas masks are needed to protect from airborne particles and sulfuric acid gas from the ports, especially when they are under positive pressure. Caution is needed when lifting sampling equipment, which is extremely heavy – close cooperation among sampling crew is advised. Additional personal protection equipment should include hard hats, safety boots and heavy duty long sleeve shirts and pants at a minimum.

Sampling crew must make sure all electrical connections are solid and grounded as well as insure that there are no frayed/damaged wires. Against the possibility of rain, all electrical connections should be secured with duct tape (insulating tape) and all receptacles should be covered or shielded. Finally, rain gear and tarps should be available to cover the meter box, sample probe, and sampling personnel.

PART II ANALYSIS OF CARBON TRAPS

This section presents practical guidance for the determination of Hg mass in exposed sorbent traps by AAS with thermal atomization.

II.1 SUMMARY OF THE METHOD

The method comprises the following steps:

- Thermal analysis of the sorbent traps content using desorption or combustion to release captured mercury for quantification;
- Transportation of mercury to the mercury analyzer by air flow;
- Direct AAS determination of mercury with Zeeman correction of background absorption.

Mercury mass is calculated from the analytical signal (peak) integration by means pre-established calibration (peak area vs. mercury mass). Mercury mass concentration will be calculated regarding the flue gas volume passed through the sorbent trap during sampling. For flue gas volume passed through the sorbent trap, please refer to PART I, Section I.8.

II.2 INTERFERENCES

There are two possible sources of interferences:

- Non-selective absorption due to the presence of destruction products originated from sample and sorbent matrices and
- Sorbent composition and sample matrix.

Zeeman background correction provides high selectivity of the mercury determination in samples with complex matrices. Special measures such as simultaneous evaluation of the background absorption should be taken to detect possible interferences. It is assumed that an increase in the background absorption up to the value of $D=2$ does not lead to a false response. It means that no sample preparation, additional oxidizers and carrier gases (e.g., oxygen, argon) are required.

Note - $D = \ln(I_0/I)$, where I_0 and I are the intensities of the analytical radiation at the inlet and outlet of the optical cell, respectively.

Interferences may result from the sorbent trap material as well as from the matrix sample. The iodine present on some sorbent traps may impair a negative measurement bias. High levels of sulfur trioxide can decrease the efficiency of mercury capture. These and other

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potential interferences are assessed by performing the analytical matrix interference test if applicable, the Hg⁰ and Hg⁺² analytical bias test and the field recovery tests.

II.3 ANALYTICAL SYSTEM

II.3.1 Instrumentation

A suitable analytical system is shown in **Error! Reference source not found.** It consists of: a mercury analyzer coupled with a thermal chamber where pyrolysis of mercury compounds takes place; a pumping unit intended for generating air flow to transfer mercury vapor to the analytical cell of the analyzer; and a PC with the installed software for data acquisition and treatment.

Mentioning any specific manufacturer or appearance of trade names in **Error! Reference source not found.** does not imply endorsement of any products. Equivalent equipment from other manufacturers could be used for the performance of this procedure based on US EPA Method 30B.

The measurement range is from 0.5 to 100,000 nanograms (ng) of mercury on the sorbent. The wide range is achieved by using several pre-defined temperature profiles (Modes).

Figure II-1: Mercury Analyzer RA-915M (Lumex Instruments) with PYRO-915+ Attachment



- 1 - Power supply and pumping unit;
- 2 - Thermal chamber unit;
- 3 - External optical unit;

- 4 - RA-915M mercury analyzer;
- 5 - PC.

II.3.2 Software

The instrument should be operated by software that provides comprehensive and easy-to-use tools to control the instrument during measurements of mercury mass in all sections of sorbent traps.

The software should support two basic user modes - calibration of the instrument including QA and QC procedures and measurement of samples. Tools should be designed for the real-time graphic and tabular visualization of the measurement results. Also for processing of the signals either to establish a calibration graph and/or function or to calculate the mercury mass in the samples using the previously established calibrations. Data should be stored on the hard drive of the PC in a database or as separate files. Data protection should be implemented as well as data integrity and consistency checks.

The example of a software package for the analytical system (see II.3.1) is RAPID® software. The essential feature of this package, which overcomes the most significant drawback of the sorbent trap method (see II.7.3), is an integrated closed-loop control system. The system provides automatic temperature profile adjustment according to the pattern of the analytical signal or background absorption level, thus ensuring the correspondence of the output signal to the calibration range.

As shown in Figure II-2, a closed-loop control system is temporarily stopping the heating process if the signal is rising too fast and/or overcoming a predefined threshold level. Therefore, even sorbent traps with high Hg load could be analyzed properly.

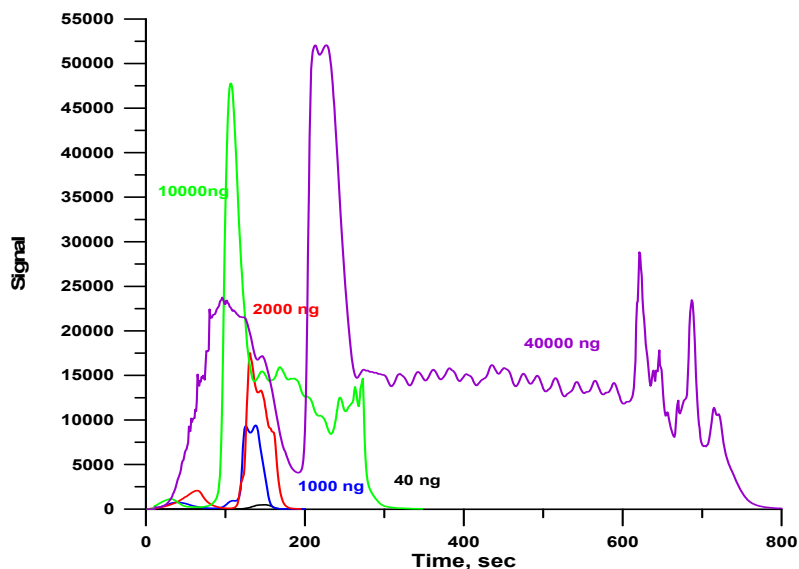


Figure II-2: Heating sequence for samples with high Hg content

II.3.3 Sorbent Traps

The sorbent media are to be configured in a trap with at least two distinct sections that can be tested separately. Section 1 is designated for the primary capture of gaseous mercury. Section 2 is designated as a backup section for determination of vapor phase mercury breakthrough. Each sorbent trap will have a unique ID (serial number) for traceability (tracking) purposes. The sorbent media may be any collection material (e.g., carbon, chemically-treated carbon) capable of quantitatively capturing and recovering mercury for subsequent analysis. The sample traps should be obtained from a reliable supplier that can demonstrate their QA and QC. Sorbent traps can be supplied with an additional spiked section intended for the Analytical Bias Test.

Dedicated sorbent traps can include a section for acid gases removal and additional two sections for speciation analysis.

Schematic diagrams of sorbent traps are given in Figure II-3.

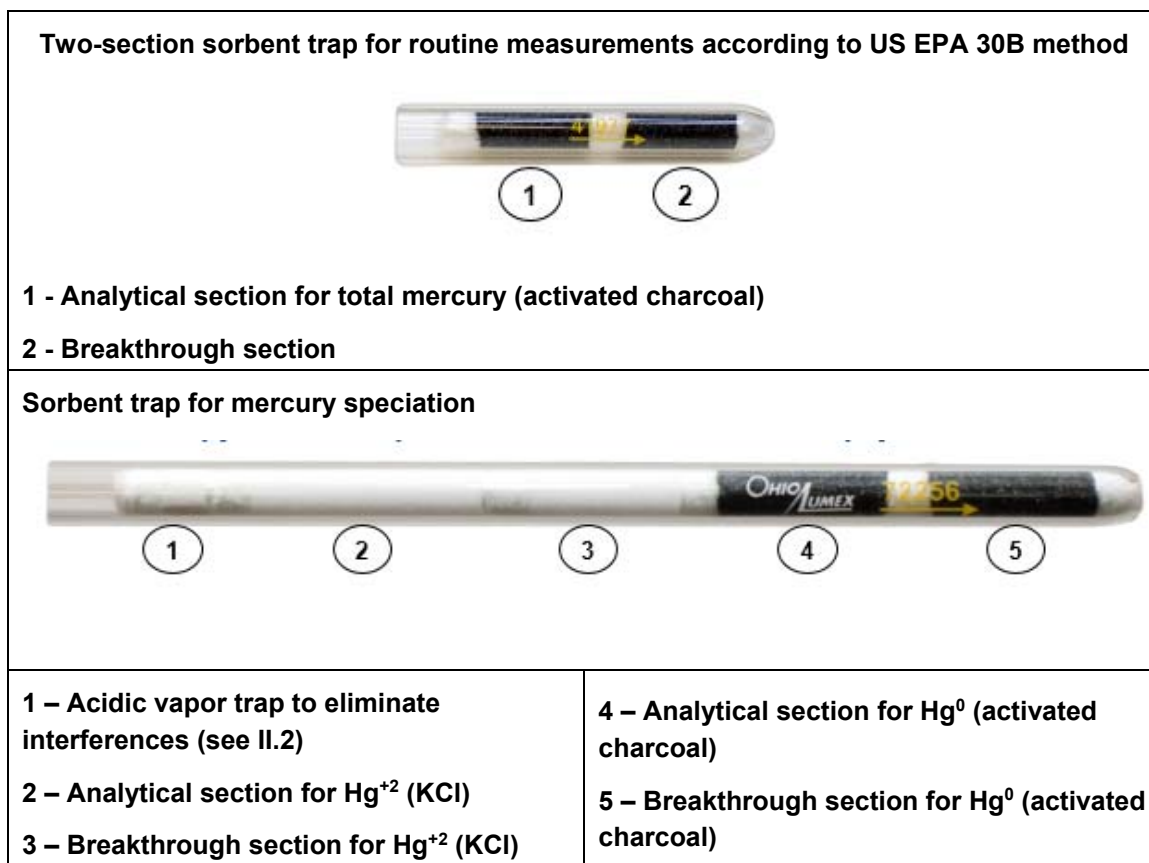


Figure II-3: Sorbent traps (gas flow direction marked by arrows is from left to right)

II.3.4 Supplies for instrument calibration

Traceable Certified Reference Material (CRM) of mercury ions solution, e.g., C(Hg)=1.0 g/L is needed for instrument calibration. Make sure the CRM is in line with the national legislation on measurements conformity.

Additional equipment may be used to prepare calibration standards from the CRM of mercury ions solution and to bring them onto the sorbent, (e.g., volumetric flasks and pipettes, micropipette systems, dispensers, analytical balance and chemical reagents).

II.4 PRE-OPERATIONAL PROCEDURES

Before starting measurements, refer to the manual for the analytical systems used and the software package. Make sure all safety requirements are met and laboratory operating conditions are in line with the manufacturer's specifications.

Any potential contamination sources (e.g., traces of mercury in the laboratory working area, on the glassware) are extremely important and should be avoided. All reusable labware in contact with the sample is to be cleaned prior to use. Clean labware must be stored in a clean area until ready for use.

Check the system for correct assembly and absence of any leakage. Heat up the analytical system and check its performance according to the manufacturer's instructions. Prior to the analysis, quartz boats must be cleaned from mercury by inserting them into the thermal chamber for 60 s. Cool down the boats before analysis to the ambient temperature.

II.5 ANALYTICAL SYSTEM CALIBRATION

Perform a multipoint calibration of the analyzer at three or more upscale points over the desired quantitative range by plotting the instrument response (i.e., peak area) of the analyzer vs mercury mass. If necessary, several calibration ranges can be established.

Take special care to ensure the analytical system is appropriately calibrated prior to sample analysis. The calibration range(s) should overlap the levels of mercury mass expected to be collected and measured. The calibration may be performed by spiking the standards onto the sorbent media and then introducing into the analyzer after preparing the sorbent/standard according to Appendix C of this document.

To create a calibration, perform the analysis of the blank (dilution solution, solution No 1 in Table II-1 and Table II-2) and calibration solutions. The recommended stock solutions for relative accuracy test audits (RATA) testing and monitoring systems based on the sorbent traps are stated in Table II-1 and Table II-2.

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Table II-1: Recommended calibration solutions while using the method for RATA

N	Mercury stock solution		
	C, µg/L	Volume, µl	Mercury mass, ng
1	0	100	0.0
2	10	100	1.0
3	100	100	10
4	1000	100	100
5	1000	100	100

Table II-2: Recommended calibration solutions for the data acquisition from emission monitoring systems based on the sorbent traps

N	Mercury stock solution		
	C, µg/L	Volume, µl	Mercury mass, ng
1	0	100	0.0
2	1	100	100
3	10	100	1,000
4	100	100	10,000
5	1000	100	100,000

Place 200 to 250 milligrams (mg) of the activated charcoal into the quartz boat (approximately 2/3 of its volume). Using a micropipette, take an aliquot of the stock solution listed in Table II-1 or Table II-2 and evenly distribute it on the top of the charcoal bed (Figure II-4). Enter the volume of the stock solution (in microliters) and the reference data to the corresponding boxes of the RAPID® software. Insert the boat into the pre-heated thermal chamber and register the output signal until its level returns to the baseline but at least 60 s.

Remove the boat with the remnants of the sample and let the boat cool up to the ambient temperature before using it for another measurement.

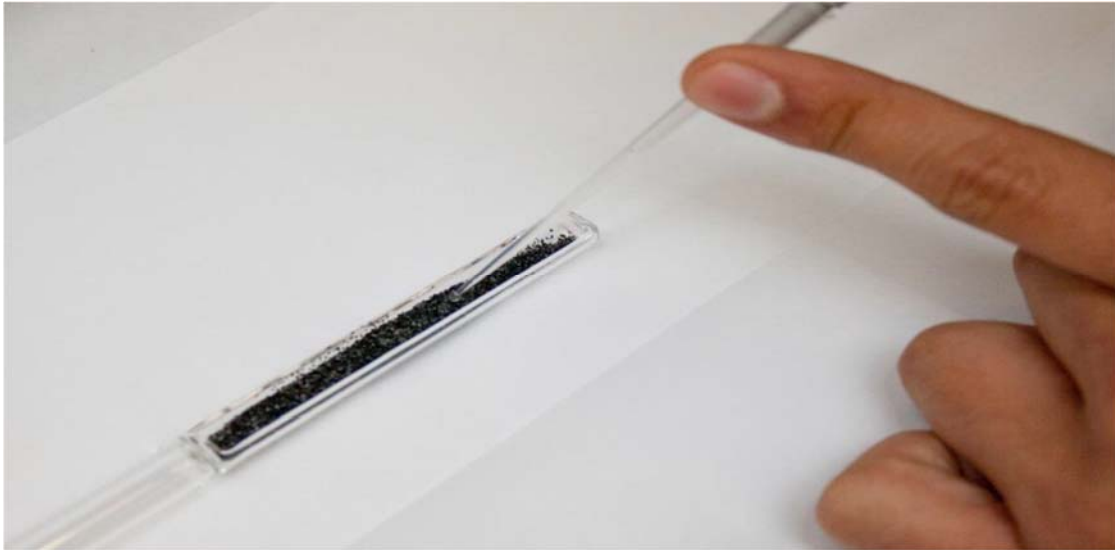


Figure II-4: Loading charcoal with mercury solution

Select all the calibration points and create the calibration graph. Check the acceptability of the calibration function using the square of the linear correlation coefficient, i.e., r^2 , which must exceed 0.99, and the analyzer response that must be within $\pm 10\%$ of the reference value at each calibration point. Reject outliers and repeat measurement if necessary.

Once performed, the calibration can be used for calculation of mercury mass in the samples provided the analysis of independent calibration standards on the day of the analysis is compliant with the acceptance criterion - the measured value of the independently prepared standard must be within $\pm 10\%$ of the expected value. Use at least two independent standards to verify the validity of the calibration. If these requirements are not met, make sure the control solution is prepared properly and repeat the validation. If the validation fails again, repeat the calibration of the instrument.

Routinely, verify the calibration function validity by conducting the Analysis of Continuing Calibration Verification Standard (CCVS) test after no more than 10 samples and at the end of each batch of samples. The use of a CCVS with the mercury content 40 to 80 % of the calibration upper limit is highly recommended. The measured value of the mercury mass in the applied standard must be within $\pm 10\%$ of the expected value.

The calibration should be repeated after instrument repair.

II.6 ANALYTICAL SYSTEM PERFORMANCE CRITERIA

II.6.1 Measurement System Performance Tests: overview

The following laboratory and field procedures and associated criteria of this section are designed to ensure:

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1. Selection of a sorbent and analytical technique combination capable of quantitative collection and analysis of gaseous mercury;
2. Collection of an adequate amount of mercury on each sorbent trap during field tests, and
3. Adequate performance of the method for each test program.

The primary objectives of these performance tests are to characterize and verify the performance of the intended analytical system and associated sampling and analytical procedures, and to define the minimum amount of mercury that can be quantified reliably:

- a. Determination of Method Detection Limit (MDL; see II.6.2.1)
- b. Determination of Minimum Sample Mass (see II.6.2.2);
- c. Analytical Bias Test (see II.6.2.3);
- d. Determination of Target Sample Volume (see II.6.2.4);
- e. Determination of Sample Run Time (see II.6.2.5);
- f. Field Recovery Test (see II.6.2.6).

II.6.2 Measurement System Performance Tests: Detailed Description

II.6.2.1 Method Detection Limit

MDL is the minimum mass of the mercury that can be detected using any particular analytical system. The MDL should be determined at least once for the analytical system using an MDL study based on the estimation of standard deviation for the blank. MDL is usually considered to be three times the standard deviation for the blank.

II.6.2.2 Determination of Minimum Sample Mass

Minimum mass of mercury is the minimum mass of mercury per sample that should be collected to ensure reliable measurement results. This information is necessary to effectively perform the Hg⁰ and Hg⁺² Analytical Bias Test and estimate target sample volumes for test runs.

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Establish a calibration function for the most sensitive calibration range. Select a mass that is no less than two times the lowest mass in your calibration, which should be at least 3.3, and preferably 10 times the MDL (see II.6.2.1).

Note 1: The level of 3.3 times the MDL is designated (compare US EPA Method 301) as the practical limit of quantitation, which is the lowest level above which quantitative results may be obtained with an acceptable degree of confidence (relative expanded uncertainty for 99% confidence level is 30 %). Assume the calibration levels are 5 ng, 10 ng, 20 ng, 50 ng, 100 ng, 200 ng. Based on two times the lowest point of the calibration function, 10 ng is selected as the minimum sample mass.

Note 2: In this example, if the typical background (blank) mercury level is relatively high (e.g., 3 ng) due to some reason, (e.g., poor quality of sorbent materials), the sample mass of 10 ng might not be sufficient to ensure that other criteria would be met, so a higher point on the calibration curve (e.g., 20 ng) should be taken as a basis for the minimum sample mass.

II.6.2.3 Analytical Bias Test

Before analysis of any field samples, the laboratory must demonstrate the ability to recover and accurately quantify Hg^0 and Hg^{+2} from the chosen sorbent media. The following analytical bias test should be performed for sorbent traps spiked with Hg^0 and Hg^{+2} at a minimum of two distinct levels that represent the lower and upper bounds of sample loadings with mercury typical for the most field samples the laboratory encounters. The minimum sample mass established in II.6.2.2 can be used for the lower bound. When establishing the upper bound, ensure it is within the calibration range.

The guidelines for this test are:

Analyze the control section of three sorbent traps containing mercury at the lower bounds of sample loadings with mercury level and the control section of three sorbent traps containing mercury at the upper bound of sample loadings. In other words, perform analysis at each level in triplicate.

Note. It is strongly recommended to use sample traps with a control section. If not, spike traps with mercury using vapor generators, gas cylinders (tanks) or CRMs of mercury solutions.

The average recovery for the three traps at each loading level must be between 90 and 110%. The test must be performed separately for Hg^0 and Hg^{+2} .

II.6.2.4 Determination of Target Sample Volume

The target sample volume is an estimate of the sample volume needed to ensure that valid emissions data are collected (i.e., sample loadings with mercury fall within the calibration range and are within the upper and lower bounds set by the analytical bias tests). The target sample volume can also be determined by performing a diagnostic test run prior to initiation of formal testing.

Example: If the minimum sample mass is 20 ng and the concentration of mercury in the stack gas is estimated to be in the whereabouts of 1 $\mu\text{g}/\text{m}^3$ (ng/L), the target sample volume is:

$$\textit{Target Sample Volume} = \frac{20 \text{ ng}}{1 \text{ ng/L}} = 20 \text{ L.} \quad (8)$$

II.6.2.5 Determination of Sample Run Time

Sample run time is a function of minimum sample mass (see II.6.2.2), target sample volume (see II.6.2.4) and nominal flow rate for the sampling equipment. The minimum sample run time for tests aiming to characterize an emission source is 1 hour. The target sample run time can be calculated using the following example.

Example: If the target sample volume has been determined to be 20 L (see II.6.2.4), the sampling time necessary to acquire 20 liters at a flow rate of 0.4 L/min is

$$\textit{Sample Run Time} = \frac{20 \text{ L}}{0.4 \text{ L/min}} = 50 \text{ min.} \quad (9)$$

II.6.2.6 Field Recovery Test

The field recovery test provides a verification of the performance of the whole analytical procedure including sampling and analysis of the exposed sampling traps. The conducting of this test requires an estimate of the stack mercury concentration at the time of testing.

II.6.2.6.1. Calculation of Pre-sampling Spiking Level

Determine the sorbent trap spiking level for the field recovery test using estimates of the stack mercury concentration, the target sample flow rate, and the planned sample duration. First, determine the mass of mercury expected to be collected in the sorbent trap. The pre-sampling spike must be within 50 to 150% of this expected mass.

Example: For an expected stack mercury concentration of 5 $\mu\text{g}/\text{m}^3$ (ng/L), a target sample flow rate of 0.40 L/min, and sampling duration of 1 hour the expected mercury mass is

$$\textit{Expected Hg mass} = 0.4 (\text{L/min}) * 60 (\text{min}) * 5 (\text{ng/L}) = 120 \text{ ng.} \quad (10)$$

A spike of 60 to 180 ng would be appropriate. Spike mercury onto the front section of the sorbent traps.

II.6.2.6.2. Conducting the test

Set up two identical sampling trains. One of the sampling trains will be designated as the spiked train and the other one as the non-spiked train. Use spiked sorbent traps in the spiked train.

Take the sample of the flue gas with the two trains simultaneously using the same procedures as for the field samples (see II.7). The total sample volume should be within $\pm 20\%$ of the target sample volume for the field sample test runs. Analyze the sorbent traps from the two trains. Determine the recovery of the spike (see II.8.6). Repeat this procedure for a total of three runs, i.e., there must be six spiked and six non-spiked sorbent traps (two parallels for both in each run). Record the individual *R* values in the test report; the average of the three *R* values must be between 85 and 115%.

II.7 FIELD SAMPLE ANALYSIS

II.7.1 Sample Collection and Handling

The sampling procedure is described in PART I of this document.

To avoid contamination of the samples, special attention should be paid to cleanliness during transport, field handling, sampling, recovery, and laboratory analysis, as well as during preparation of the sorbent cartridges. Collection and analysis of blank samples (e.g., reagent, sorbent) is useful in verifying the absence of the source of contaminant mercury.

Proper procedures and documentation for sampling are critical to ensuring data integrity and therefore will be applied to all samples including field samples and blanks.

II.7.2 Sample Preparation

Combine for analysis all materials associated with each section; any supporting substrate that the sample gas passes through prior to entering a media section should be analyzed with that segment. Protective gloves should be used at all time during sample preparation.

Use a cutting tool with a diamond disk or a manual tool to cut the trap just above the first plug (Figure II-5-1), break glass open (Figure II-5-2) and remove the plug with the glass wool extractor (Figure II-5-3).

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Fig. II-5-1



Fig. II-5-2



Fig. II-5-3

Figure II-5: Opening sorption trap

Carefully remove the glass wool plug with tweezers (Figure II-6-1) and discharge sorbent on a fresh sheet of printer paper (Figure II-6-2).

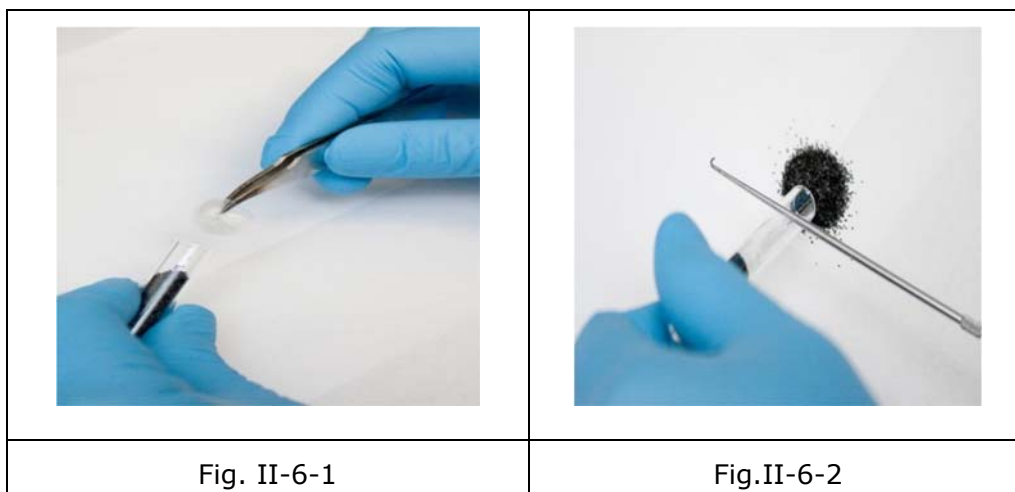


Figure II-6: Removing glass wool plug

Wrap up the glass wool plug in a small piece of aluminum foil (Figure II-7-1). Be sure no glass wool is exposed (Figure II-7-2).

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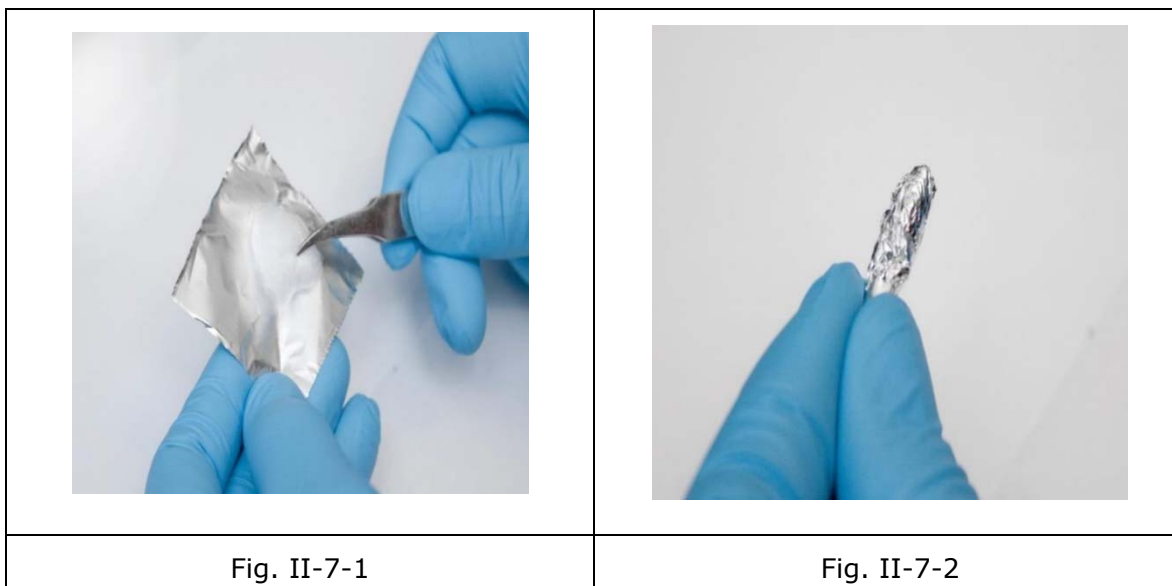


Figure II-7: Wrapping glass wool plug

Quantitatively transfer the sorbent from each section of the trap into separate quartz boats. Place the corresponding plug into the boat along with the sorbent. Use the second sheet of printer paper placed under the boat to catch any spilled sorbent (Figure II-8).

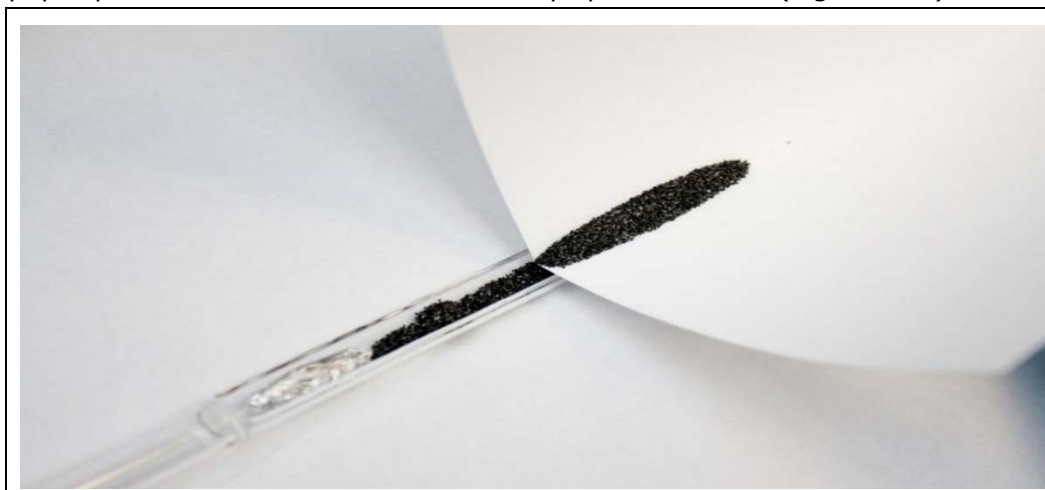


Figure II-8: Transferring the sorbent into a quartz boat

II.7.3 Sample analysis

Enter the sample description (ID) and put the boat inside the pre-heated thermal chamber. Register the output signal until its level returns to the baseline but at least 60 seconds. Should be no peak available, extend the time as much as 100 seconds. Integrate the signal and use it to calculate the mercury mass.

Method for Determination of Hg Concentration in Stack Gas Using Carbon Traps

Remove the boat with the remnants of the sample and let the boat cool up to the ambient temperature before using it for another measurement.

For every standard trap two values should be acquired for further calculations:

- Hg mass in Section 1 (analytical section);
- Hg mass in Section 2 (breakthrough section).

For every spiked 3-section trap three values should be acquired for further calculations:

- Hg mass in Section 1 (analytical section);
- Hg mass in Section 2 (breakthrough section);
- Hg mass in Section 3 (spiked section).

For every speciation 4-section trap four values should be acquired for further calculations:

- Hg⁺² mass in Section 1 (analytical section for ionic mercury);
- Hg⁺² mass in Section 2 (breakthrough section for oxidized mercury);
- Hg⁰ mass in Section 1 (analytical section);
- Hg⁰ mass in Section 2 (breakthrough section).

Hg mass in sorbent trap Section 1 for all samples must be within the calibrated range of the analytical system.

Be aware samples that are not within the calibrated range cannot be re-analyzed. As a result, the sample cannot be validated, and another sample must be collected. It is strongly suggested that the analytical system should be calibrated over multiple ranges (or over a single wide range, if the instrument permits) so analyzed samples do fall within the calibrated range. A special feature of the advanced system (see II.3.2) is an integrated closed-loop control system that can adjust the sensitivity of the instrument in respect to the mercury content.

Furthermore, the total mass of mercury measured in Section 1 of each sorbent trap must also fall within the lower and upper mass limits established during the initial Hg⁰ and Hg⁺² analytical bias test. If a sample is analyzed and found to fall outside of these limits, it is acceptable to perform an additional analytical bias test for Hg⁰ and/or Hg⁺² that now includes this level.

However, some samples (e.g., the mass collected in trap Section 2 or the mass collected in trap Section 1 when the Hg stack gas concentration is <0.5 µg/m³), may have Hg levels so low that it may not be possible to quantify them in the calibrated range of the analytical system. Because a reliable estimate of these low-level measurements is necessary to fully validate the emissions data, the MDL (see II.6.2.1) is used to establish the minimum mass that can be detected and reported.

Method for Determination of Hg Concentration in Stack Gas Using Carbon Traps

If the measured mass is below the lowest point in the calibration curve and above the MDL, analyze an additional calibration standard in between the MDL and the lowest calibration point. Use the instrument response to estimate the Hg mass by calculating a response factor (i.e., peak area per mass or concentration) and estimate the mass of mercury present in the sample based on the analytical response for this sample and the response factor.

Example: The analysis of a particular sample results in a measured mass above the MDL, but below the lowest point in the calibration curve which is 10 ng. An MDL of 1.3 ng Hg has been established by the MDL study. A calibration standard containing 5 ng of Hg is analyzed producing a response of 6,170 (peak area, arbitrary units), which equates to a response factor of 1,234 area units/ng. The analytical response for the sample is 4,840 area units. Dividing the analytical response for the sample by the response factor gives 3.9 ng, which is the estimated mass of Hg in the sample.

II.7.4 Analysis of Blanks

The analysis of blanks is optional but it is useful to verify the absence of, or an acceptable level of, Hg contamination.

Analyze from time to time (e.g. when you are starting a new batch or change a supplier of sorbent traps or in a case of doubtful or inconsistent measurement results) unexposed sorbent traps.

Blank levels should be considered when quantifying low Hg levels and their potential contribution to meeting the sorbent trap section 2 breakthrough requirements. However, correcting sorbent trap results for blank levels is not allowed.

II.8 CALCULATIONS AND DATA ANALYSIS

II.8.1 Calculation of Spike Recovery (Analytical Bias Test)

Calculate the recovery of Hg⁰ and Hg⁺² using Equation (11)

$$R = \frac{m_{\text{recovered}}}{m_{\text{spiked}}} \cdot 100 . \quad (11)$$

II.8.2 Calculation of Breakthrough

Calculate the breakthrough of Hg to the second section of the sorbent trap using Equation (12)

$$B = \frac{m_2}{m_1} \cdot 100 . \quad (12)$$

II.8.3 Calculation of mercury concentration in the sample

Calculate the Hg concentration in the sample measured with sorbent trap "a" (the former one between paired sorbent traps) using Equation (13)

$$C_a = \frac{m_1 + m_2}{V_t} \cdot 100. \quad (13)$$

For sorbent trap "b" (the latter one between paired sorbent traps), replace "C_a" with "C_b" in Equation (13). Report the average concentration, i.e., $\frac{1}{2} (C_a + C_b)$.

Note. In Equations (1) to (7), C_a (C_b) is denoted as [Hg].

II.8.4 Moisture Correction

Use Equations (3) to (5) if measurements need to be corrected to a wet basis.

II.8.5 Calculation of Paired Trap Agreement

Calculate the relative deviation (RD) between the Hg mass concentrations measured with the paired sorbent traps using Equation (14)

$$RD = \frac{|C_a - C_b|}{C_a + C_b} \cdot 100 \quad (14)$$

II.8.6 Calculation of Measured Spike Hg Concentration (Field Recovery Test)

Calculate the measured spike concentration using Equation (15)

$$C_{rec} = \frac{m_s}{V_s} - \frac{m_u}{V_u}. \quad (15)$$

Then calculate the recovery, *R*, using Equation (16)

$$R = \frac{C_{rec} \cdot V_s}{m_{spiked}} \cdot 100. \quad (16)$$

II.9 QUALITY ASSURANCE AND QUALITY CONTROL

Table II-3 shows QA/QC criteria related to the measurement of the Hg mass after field sampling using sorbent trap tubes. Criteria for sampling are given in PART I, Section I.7.

Table II-3: Quality Assurance/Quality Control Criteria for Analysis

QA/QC Test or Specification	Acceptance Criteria	Frequency	Consequences if Not Met
Analytical Bias Test	Average recovery between 90% and 110% for Hg ⁰ and Hg ⁺² at each of the two concentration levels	Prior to use of new sorbent media	Field samples will not be analyzed until the percent recovery criteria has been met
Multipoint analyzer calibration acceptance test	The analyzer reading within $\pm 10\%$ of true value and $r^2 \geq 0.99$	After calibration of the instrument has been performed	Recalibrate the analyzer
Analysis of independent calibration standards	The analyzer reading within $\pm 10\%$ of true value	On the day of analysis before starting analysis of samples	Recalibrate the analyzer and check the acceptance of the calibration
Analysis of CCVS	The analyzer reading within $\pm 10\%$ of true value	After analysis of 10 samples	Recalibrate the analyzer and check the acceptance of the calibration. Samples analyzed after the last successful CCVS test are invalidated

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QA/QC Test or Specification	Acceptance Criteria	Frequency	Consequences if Not Met
Sorbent trap section 2 breakthrough	<p>Mercury mass $\leq 10\%$ of that in section 1 of the sorbent trap if mercury concentration in the sample is $> 1 \mu\text{g/dscm}$</p> <p>Mercury mass $\leq 20\%$ of that in section 1 of the sorbent trap if mercury concentration in the sample is $\leq 1 \mu\text{g/dscm}$</p>	Each sample	Sample is invalidated. Data from the pair of sorbent traps are also invalidated
Paired sorbent traps repeatability	<p>Relative deviation of mercury mass $\leq 10\%$ if mercury concentration in the sample is $> 1 \mu\text{g/dscm}$</p> <p>Relative deviation of mercury mass $\leq 20\%$ if mercury concentration in the sample is $\leq 1 \mu\text{g/dscm}$</p>	Each run	Run invalidated
Sample analysis	Mercury mass is within the calibration range	Each sample	Sample is invalidated
Sample analysis	Mercury mass is within the bounds of Analytical Bias Test	Each sample	Expand boundaries of Analytical Bias Test. If not, sample is invalidated
Field recovery test	Average recovery between 85% and 115% for Hg^0	Once per field test	Field sample runs not validated without successful field recovery test

II.10 GUIDELINES ON METHOD VALIDATION

It is the user's ultimate responsibility to perform validation of this method in their laboratory and maintain the quality of analytical results.

Measurement data are validated using initial, onetime laboratory tests coupled with everyday tests and procedures. The tests laid down in II.6.2.1 - II.6.2.6 are deemed to be the core part of the initial tests for the analytical procedure. They should be merged with the validation procedures and tests for sampling, as described in PART I, Section I.7.

To maintain and prove the ability to perform routine measurements, tests should be set out on a daily basis (see II.9). Participation in interlaboratory validation and proficiency testing programs is also of great importance.

II.11 SAFETY CONSIDERATIONS FOR ANALYSIS

It is essential that analytical tests conducted according to the procedure described here are carried out by suitably qualified staff. Hg and its compounds are very toxic. Extreme caution should be exercised when handling samples and solutions, which contain or may contain Hg. The procedure described here does not purport to address all of the safety problems that may be associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

Policies should be in place to minimize the risk of chemical exposure and to properly handle waste disposal in the laboratory. Personnel should wear appropriate laboratory attire and personal protection equipment, according to protocols established by the laboratory.

Any wastes generated by this procedure must be disposed of according to the hazardous material management plan that details and tracks various waste streams and disposal procedures.

APPENDIX A

Sampling Data Sheet



SINGLE POINT CONSTANT RATE SAMPLING DATA SHEET

PLANT NAME		TUBE TRAP NUMBER			RUN NUMBER		
PLANT LOCATION - CITY/STATE					DATE	OPERATOR	
SAMPLING LOCATION					RUN START/STOP TIME		
P _b (inches Hg)	METER BOX		SAMPLE TRAIN LEAK CHECK				
	NUMBER	GAMMA (γ)	INITIAL		FINAL		
			inches Hg	LPM	inches Hg	LPM	
ELAPSED TIME (minutes)	DGM READING (liters)		ROTAMETER SETTING (liters/minute)	DGM TEMP. (°C)	PROBE TEMP. (°C)	STACK TEMP. (°C)	H ₂ O TRAIN TEMP. (°C)
0/Initial							
5							
10							
15							
20							
25							
30							
35							
40							
45							
50							
55							
60/Final			Avg.	Avg.	Avg.	Avg.	Avg.

APPENDIX B

Chain of Custody Record



CHAIN OF CUSTODY RECORD

Project Name	
Project Location	
Sampling Location	
Project Number	
Laboratory	
Laboratory P.O. #	

Sample ID	Sample Matrix	Analysis Requested

Notes/Comments:	
Please hold canisters for pickup and delivery to another lab for further analyses. Notify when complete.	

Relinquished by:		Relinquished by:	
Date/Time:		Date/Time:	
Received by:		Received by:	
Date/Time:		Date/Time:	

APPENDIX C

Preparation of calibration solutions and auxiliary solutions



C.1 General

Mercury calibration solutions should be prepared from a CRM which is traceable to national or international reference(s).

Additional equipment and labware may be in use to prepare calibration standards from CRM of mercury ions solution and to bring them onto the sorbent. It includes volumetric flasks, volumetric pipettes, micropipette systems, dispensers, analytical balance etc. as well as chemical reagents. Use chemical reagents of recognized analytical grade preferably intended for mercury trace analysis. Consult your supplier before placing an order.

Unless otherwise specified, use water of grade 1 according to ISO 3696. Check contamination of water with mercury on regular basis.

C.2 Cleaning of glassware

All the glassware and should be cleaned using hot water and then with heated nitric acid solution (C.3.2) or chromic mixture (C.3.1). Strongly contaminated pieces of glassware are to be soaked in chromic mixture for 12-24 hours. After that the glassware should be thoroughly washed with distilled water.

C.3 Preparation of auxiliary solutions

C.3.1 Chromic mixture

Carefully dissolve 10 g of potassium dichromate ($K_2Cr_2O_7$, p.) in 100 mL of the concentrated sulfuric acid (p.). Some residue of the initial potassium dichromate is allowed. Chromic mixture should be kept in a dark glass vessel.

C.3.2 Nitric acid solution

Carefully add with stirring 500 mL of the concentrated nitric acid ($d=1.37$ g/mL) to 500 mL of distilled water.

C.3.3 Dilution solution

Place 500-600 mL of distilled water in a volumetric flask of 1000 mL capacity, add 200 mg of potassium dichromate ($K_2Cr_2O_7$, p.a.) and mix until complete dissolution. Then carefully add with stirring 50 mL of concentrated nitric acid ($d=1.37$ g/mL). After cooling dilute the mixture up to the mark.

The solution is stable for 3 months if kept in the dark place.

Check this solution on mercury contamination according to the recommendations of the analytical system manufacturer before use.

C.4 Preparation of mercury solutions

C.4.1 Mercury stock solution C(Hg)=100 mg/L (nominal concentration)

Place 3-5 mL of the dilution solution (C.3.3) in a 10 mL volumetric flask. Then place 1 mL of the CRM of mercury ions solution (C(Hg)=1.0 g/L). Bring the contents of the flask up to the mark with the dilution solution and stir thoroughly. Calculate assigned value of the mercury mass concentration in the prepared solution as given by Equation (C.1).

$$C_{ref} = C_{Cer} \cdot \frac{V_A}{V_K}, \quad (C.1)$$

Where

C_{Ref} is the assigned (reference) value of the mercury mass concentration in the prepared solution, mg/L;

C_{Cer} is the certified value of the mercury mass concentration in the CRM of the mercury ions, mg/L;

V_A is the volume of the aliquot portion of the CRM, mL;

V_K is the volume of the volumetric flask, mL.

The solution is stable for 6 months if kept in a fridge (2 to 8 °C).

C.4.2 Mercury stock solution C(Hg)=10.0 mg/L (nominal concentration)

Place 30 mL of the dilution solution (C.3.3) in a 200 mL volumetric flask. Then place 2 mL of the CRM of mercury ions solution (C(Hg)=1.0 g/L). Bring the contents of the flask up to the mark with the dilution solution and stir thoroughly. Calculate assigned value of the mercury mass concentration in the prepared solution using Equation (C.1).

The solution is stable for 6 months if kept in a fridge (2° to 8 °C).

C.4.3 Mercury stock solution C(Hg)=1000 µg/L (ppb)

Place 30 mL of the dilution solution (C.3.3) in a 50 mL volumetric flask. Then place 5 mL of the mercury stock solution C(Hg)=10.0 mg/L (C.4.2). Bring the contents of the flask up to the mark with the dilution solution and stir thoroughly.

Calculate assigned value of the mercury mass concentration in the prepared solution as follows:

$$C_{ass} = 1000 \cdot C_{ini} \cdot \frac{V_A}{V_K}, \quad (C.2)$$

Where

C_{ini} is the assigned (reference) value of the mercury mass concentration in the initial solution, mg/L;

C_{ass} is the assigned (reference) value of the mercury mass concentration in the prepared solution, µg/L;

V_A is the volume of the aliquot portion of the initial solution, mL;

V_K is the volume of the volumetric flask, mL.

The solution is stable for three months if kept in a fridge (2 to 8 °C).

C.4.4 Mercury stock solution $C(\text{Hg})=100 \mu\text{g/L}$ (ppb)

Place 30 mL of the dilution solution (C.3.3) in a 100 mL volumetric flask. Then place 1 mL of the mercury stock solution $C(\text{Hg})=10.0 \text{ mg/L}$ (C.4.2). Bring the contents of the flask up to the mark with the dilution solution and stir thoroughly. Calculate assigned value of the mercury mass concentration in the prepared solution using Equation (C.2).

The solution is stable for 3 months if kept in a fridge (2 to 8 °C).

C.4.5 Mercury stock solution $C(\text{Hg})=10 \mu\text{g/L}$ (ppb)

Place 30 mL of the dilution solution (C.3.3) in a 100 mL volumetric flask. Then place 10 mL of the mercury stock solution $C(\text{Hg})=100 \mu\text{g/L}$ (C.4.4). Bring the contents of the flask up to the mark with the dilution solution and stir thoroughly. The solution is stable for 1 month if kept in a fridge (2 to 8 °C).

Calculate assigned value of the mercury mass concentration in the prepared solution using Equation (C.2).

The solution is stable for one month if kept in a fridge (2 to 8 °C).

Note. When calculating the assigned value using Equation (C.2), be aware the mass concentration of the initial solution is expressed as milligram per liter (mg/L), i.e. 0.1 mg/L. The use of microgram per liter ($\mu\text{g/L}$) will result in error.
