



*California Environmental Protection Agency*

**AIR RESOURCES BOARD**

## Method 423

# Determination of Particulate and Gaseous Inorganic Arsenic Emissions From Stationary Sources

Adopted: January 22, 1987

## Method 423 – Determination of Particulate and Gaseous Inorganic Arsenic Emissions From Stationary Sources

### 1. APPLICABILITY AND PRINCIPLE

#### 1.1 Applicability:

This method applies to the determination of inorganic arsenic (As) emissions from stationary sources.

#### 1.2 Principle.

Particulate and gaseous arsenic emissions are withdrawn isokinetically from the source and collected on a low-background glass fiber filter and in water. The collected arsenic is then analyzed by atomic absorption spectrophotometry.

### 2. RANGE AND SENSITIVITY

The detection limits, optimum range and sensitivity will vary with the make or model of the atomic absorption spectrophotometer. However, the optimum concentration range is typically 2 to 20 ug/L for the flame arsine generation method. The lower detection limit is 0.8 ug/L (10.5).

### 3. INTERFERENCES

#### 3.1 Analysis.

Background absorption is overcome by using a deuterium or hydrogen background corrector. High concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver can cause analytical interferences. Elemental arsenic and many of its compounds are volatile and therefore As may be lost from certain samples during sample preparation (10.5).

### 4. APPARATUS

#### 4.1 Sampling Train.

A schematic diagram of the sampling train is shown in Figure 423-1. This is similar to the CARB Method 5 sampling train. The sampling train consists of the following components:

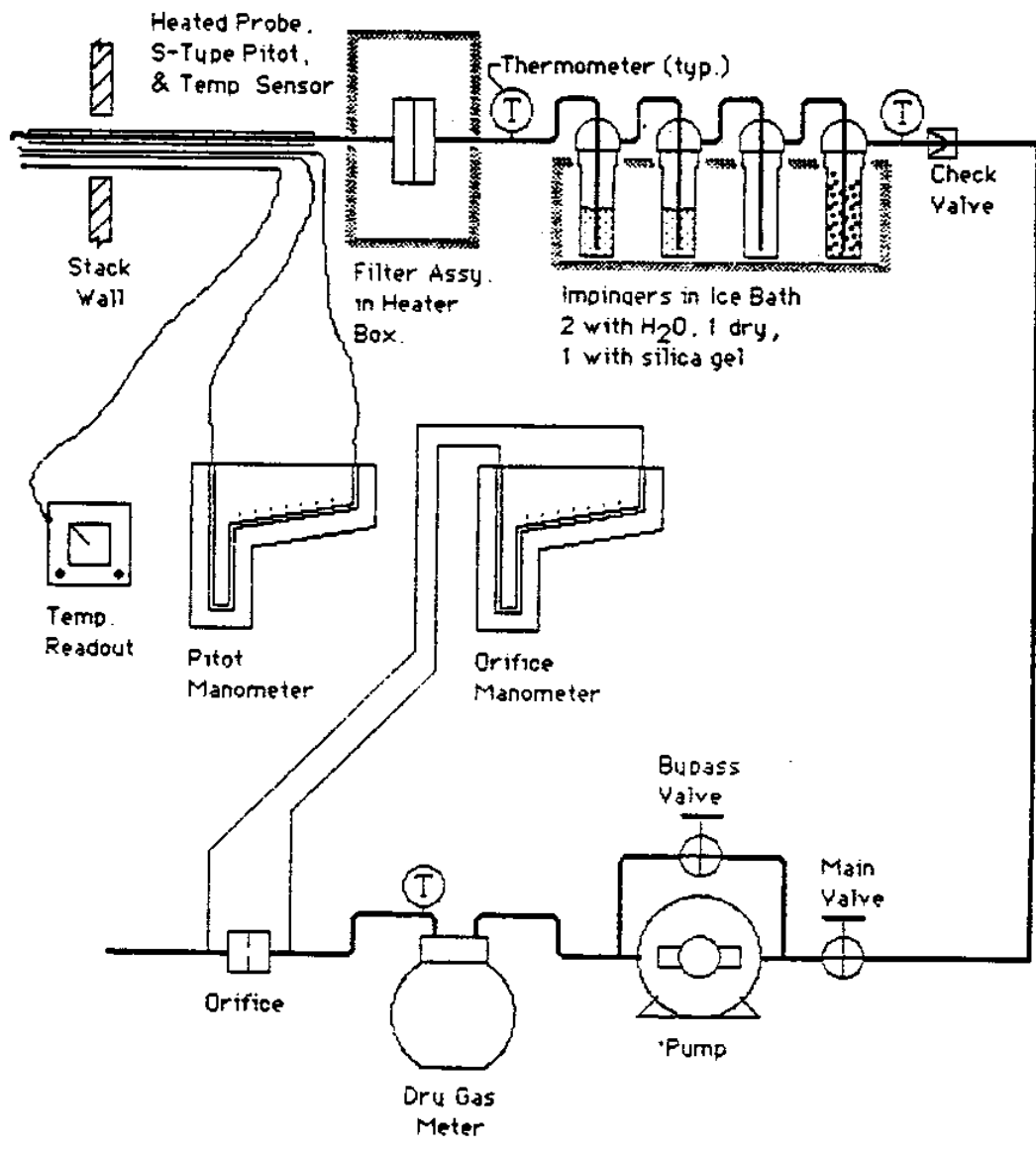


Figure 423-1 Arsenic Sampling Train

- 4.1.1 Probe Nozzle, Probe Liner, Pitot Tube, Differential Pressure Gauge, Filter Holder, Filter Heating System, Metering System, Barometer and Gas Density Determination Equipment. Same as CARB Method 5, Sections 2.1.1 to 2.1.6 and 2.1.8 to 2.1.10, respectively.
- 4.1.2 Impingers. Four impingers are connected in series with leak-free ground glass fittings or any similar leak-free non-contaminating fittings. The first, third, and fourth, are of the Greenburg-Smith design modified by replacing the tip with a 1.3 cm (0.5 in) I.D. glass tube extending to about 1.3 cm (0.5 in) from the bottom of the flask. The second impinger is of the Greenburg-Smith design with the standard tip.

The tester may use modifications (e.g. flexible connections between the impingers, materials other than glass, or flexible vacuum lines to connect the filter holder to the impinger train) subject to approval by the Executive Officer. The first and second impingers shall contain known quantities of water (Section 6.1.3), the third, shall be empty, and the fourth shall contain a known weight of silica gel or equivalent desiccant.

A thermometer capable of measuring temperature to within 1°C (2°F) should be placed at the outlet of the sixth impinger.

#### 4.2 Sample Recovery.

The following items are needed:

- 4.2.1 Probe-Liner and Probe Nozzle Brushes, Petri Dishes, Graduated Cylinder or Balance, Plastic Storage Containers, Rubber Policeman and Funnel. Same as CARB Method 5, Sections 2.2.1 and 2.2.4 to 2.2.8, respectively.
- 4.2.2 Wash Bottles. Polyethylene
- 4.2.3 Sample Storage Containers. Chemically resistant polyethylene or polypropylene for glassware washes. 500- or 1000-mL.

#### 4.3 Analysis

The following equipment is needed:

- 4.3.1 Atomic absorption spectrophotometer. Equipped with an electrodeless discharge lamp and a background corrector to measure absorbance at 193.7 nm. For measuring samples having

less than 10 ug As/mL, use a vapor generator accessory or a graphite furnace.

- 4.3.2 Recorder. To match the output of the spectrophotometer.
- 4.3.3 Beakers. 150 mL.
- 4.3.4 Volumetric Flasks. Glass, 50-, 100-, 200-, 500-, and 1,000-mL 24 and polypropylene, 50-mL.
- 4.3.5 Balance. To measure within 0.5 g.
- 4.3.6 Volumetric Pipets. 1-, 2-, 3-, 5-, 8-, and 10-mL.
- 4.3.7 Oven.
- 4.3.8 Hot plate.
- 4.3.9 Balance - Analytical capable of accurately weighing to the nearest 0.0001g.

## 5. REAGENTS

Unless otherwise specified use American Chemical Society reagent grade (or equivalent) chemicals throughout.

### 5.1 Sampling:

The following reagents are needed:

- 5.1.1 Filters, high purity glass fiber filter such as Gelman A/E (acid extracted) or equivalent.
- 5.1.2 Silica gel, Crushed Ice, and Stopcock Grease. Same as CARB Method 5, Sections 3.1.2, 3.1.4 and 3.1.5, respectively.
- 5.1.3 Water. Deionized distilled, to conform to ASTM Specification D1133-74 Type 3 (10.3). If high concentrations of organic matter are not expected to be present, the analyst may omit the potassium permanganate test for oxidizable organic matter.

### 5.2 Sample Recovery.

0.1N sodium hydroxide (NaOH) is required. Dissolve 4.0 g of NaOH in about 500 mL of water in a 1-liter volumetric flask. Then dilute to 1.0 liter with water.

### 5.3 Analysis.

The reagents needed for analysis are as follows:

5.3.1 Water. Same as 5.1.2.

5.3.2 Sodium Hydroxide 0.1N. Same as 5.2.

5.3.3 Sodium borohydride ( $\text{NaBH}_4$ ), 5 Percent (W/V). Dissolve 5.0 g of  $\text{NaBH}_4$  in about 500 mL of 0.1N NaOH in a 1-liter volumetric flask. Then, dilute to 1.0 liter with 0.1N NaOH.

5.3.4 Hydrochloric Acid (HCl). Concentrated (12M).

5.3.5 Potassium Iodide (KI), 30% percent (W/V). Dissolve 300 g of KI in 500 mL of water in a 1-liter volumetric flask. Then, dilute to 1.0 liter with water.

5.3.6 Nitric Acid ( $\text{HNO}_3$ ), Concentrated (16M).

5.3.7 Nitric Acid, 0.8 N. Dilute 52 mL of concentrated  $\text{HNO}_3$  to 1.0 liter with water.

5.3.8 Nitric Acid, 50 Percent (V/V). Add 50 mL concentrated  $\text{HNO}_3$  to 50 mL water.

5.3.9 Stock Arsenic Standard, 1 mg As/mL. Dissolve 1.3203 g of primary standard grade  $\text{As}_2\text{O}_3$  in 20 mL of 0.1N NaOH in a 150 mL beaker. Slowly add 30 mL of concentrated  $\text{HNO}_3$ . Heat the resulting solution and evaporate just to dryness. Transfer the residue quantitatively to a 1-liter volumetric flask and dilute to 1.0 liter with water.

5.3.10 Arsenic working solution, 1.0 ug As/mL. Pipet 1.0 mL of stock arsenic standard into an acid-cleaned, appropriately labelled 1-liter volumetric flask containing about 500 mL of water and 5 mL of concentrated  $\text{HNO}_3$ . Dilute to 1.0 liter with water.

5.3.11 Air. Suitable quality for atomic absorption analysis. Air may be supplied from a compressed air line, a laboratory compressor, or from a cylinder of compressed air, or as recommended by the instrument manufacturer.

5.3.12 Acetylene. Suitable quality for atomic absorption analysis. Commercial grade acetylene or as recommended by the manufacturer.

- 5.3.13 Nickel nitrate, 5 Percent ( $WNi^{2+}/V$ ). Dissolve 24.780 g of nickel nitrate hexahydrate in water in a 100-mL volumetric flask and dilute to 100 mL with water.
- 5.3.14 Nickel nitrate, 1 percent ( $WNi^{2+}/V$ ). Pipet 20 mL of 5 percent nickel nitrate solution (5.3.13) into a 100-mL volumetric flask and dilute to 100 mL with water.
- 5.3.15 Hydrogen peroxide, 3 percent. Pipet 50 mL of 30 percent hydrogen peroxide into a volumetric flask and dilute to 500 mL with water.
- 5.3.16 Quality Assurance Audit Samples. Arsenic samples prepared by the Environmental Protection Agency's (EPA) Environmental Systems Laboratory, Quality Assurance Division, Source Branch, Mail Drop 77A, Research Triangle Park, North Carolina 27711. Each set will consist of two vials of unknown concentrations. Only when making compliance determinations, obtain an audit sample set from the Quality Assurance Management Office at each EPA regional office or the responsible enforcement office.

NOTE: The tester should notify the Quality Assurance Office or the responsible enforcement agency at least 30 days prior to the test date to allow sufficient time for delivery.

## 6. PROCEDURE

### 6.1 Sampling:

Because of the complexity of the method, testers must be trained and experienced with the test procedures in order to obtain reliable results.

- 6.1.1 Pretest Preparation. Follow the same general procedure given in CARB Method 5, Section 4.1.1, except the filter need not be weighed.
- 6.1.2 Preliminary Determinations. Follow the same general procedure given in CARB Method 5, Section 4.1.2. except select the nozzle size to maintain isokinetic sampling rates below 28 liters/min (1.0 cfm).
- 6.1.3 Preparation of Collection Train. Follow the same general procedure given in CARB Method 5, Section 4.1.3.
- 6.1.4 Leak-Check Procedures. Follow the general leak-check procedures given in CARB Method 5, Sections 4.1.4.1 (Pretest

Leak Check), 4.1.4.2 (Leak-Checks During the Sample Run), and 4.1.4.3 (Post-Test Leak-Check).

6.1.5 Arsenic Sampling Train Operation. Follow the general procedure given in CARB Method 5, Section 4.1.5. except maintain a temperature of 107° to 135°C (225° to 275°F) around the filter and maintain isokinetic sampling flow rates below 28 liters/min (1.0 cfm). For each run, record the data required on a data sheet such as the one shown in Figure 423-2.

6.1.6 Calculation of Percent Isokinetic. Same as CARB Method 5, Section 4.1.6.

## 6.2 Sample Recovery.

Begin proper clean-up procedure as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it. Do not cap off the probe tip tightly while the sampling train is cooling as this would create a vacuum in the filter holder, thus drawing liquid from the impingers into the filter.

Before moving the sampling train to the cleanup site, remove the probe from the sampling train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the filter inlet where the probe was fastened and cap it. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger or condenser and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the impingers or condenser. After wiping off the silicone grease, cap off the filter holder outlet and impinger inlet. Either ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

Transfer the probe and filter-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized. Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:



- 6.2.1 Container No. 1 (Filter). Carefully remove the filter from the filter holder and place it in its identified petri dish container. Use a pair of tweezers or clean disposable surgical gloves or both to handle the filter. If it is necessary to fold the filter, fold the particulate cake inside the fold. Carefully transfer to the petri dish any particulate matter and filter fibers that adhere to the filter holder gasket by using a dry nylon bristle brush and/or a sharp-edged blade. Seal the container.
- 6.2.2 Container No. 2 (Probe). Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fittings, probe liner, and from half of the filter holder by washing these components with 0.1N NaOH and placing the wash in a plastic storage container. Measure and record to the nearest mL the total volume of solution in Container No. 2. Perform the rinsing with 0.1N NaOH as follows:

Carefully remove the probe nozzle and rinse the inside surfaces with 0.1N NaOH from a wash bottle. Brush with a nylon bristle brush and rinse until the 0.1N NaOH rinse shows no visible particles. Then make a final rinse of the inside surface.

Brush and rinse the inside parts of the Swagelok fitting with 0.1N NaOH in a like manner until no visible particles remain.

Rinse the probe liner with 0.1N NaOH. While squirting 0.1N NaOH into the upper end of the probe, tilt and rotate the probe so that all inside surfaces will be wetted with the rinse solution. Let the 0.1N NaOH drain from the lower end into the sample container. The tester may use a glass or polyethylene funnel to aid in transferring liquid washes to the container. Follow the rinse with a probe brush. While holding the probe in an inclined position, squirt 0.1N NaOH into the upper end of the probe and at the same time, push the probe brush with a twisting action through the probe. Hold the sample container underneath the lower end of the probe, and catch any liquid and particulate matter brushed from the probe. Run the brush through the probe three or more times until no visible particulate matter is carried out with the rinse and none remains on the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times, since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with 0.1N NaOH and quantitatively collect these washings in the sample container. After the brushing, make a final rinse of the probe as described above.

It is recommended that two people clean the probe to minimize loss of sample.

Between sampling runs, keep brushes clean and protected from contamination.

After ensuring that all joints have been wiped clean of silicone grease, brush and rinse the inside of the front half of the filter holder with 0.1N NaOH. Brush and rinse each surface three times or more, if needed, to remove visible particulate matter. Make a final rinse of the brush and filter holder. Carefully brush and rinse out the glass cyclone also if applicable. After all washings and particulate matter have been collected in the sample container, tighten the lid so that liquid will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to clearly identify its contents.

Rinse the glassware a final time with water to remove residual NaOH before reassembling. Do not save the final rinse water.

6.2.3 Container No. 3 (Silica Gel). Check the color of the indicating silica gel to determine whether it has been completely spent, and note its condition. Transfer the silica gel from the fourth impinger to the original container, and seal. The tester may use a funnel to pour the silica gel, and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of particles that may adhere to the impinger walls and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, the tester may follow the procedure for Container No. 3 in Section 6.5 (Analysis).

6.2.4 Container No. 4 (Impinger Water). Clean each of the first two impingers and connecting glassware in the following manner.

- a) Wipe the impinger ball joints free of silicone grease and cap the joints.
- b) Weigh the impinger and liquid to within  $\pm 0.5$  g. Record in the log the weight of the liquid present, and note any color or film observed in the impinger catch. The weight of liquid is needed along with the silica gel data to calculate the stack gas moisture content.

- c) Rotate and agitate each impinger using the impinger contents as a rinse solution.
- d) Transfer the liquid to Container No. 4. Remove the outlet ball-joint cap, and drain the contents through this opening. Do not separate the impinger parts (inner and outer tubes) while transferring their contents to the cylinder.

Note: In steps e and f below, measure and record the total amount of 0.1N NaOH used for rinsing.

- e) Pour approximately 30 mL of 0.1N NaOH into each of the first two impingers and agitate the impingers. Drain the 0.1N NaOH through the outlet arm of each impinger into Container No. 4. Repeat this operation a second time; inspect the impingers for any abnormal conditions.
- f) Wipe the ball joints of the glassware connecting the impingers and the back half of the filter holder free of silicone grease, and rinse each piece of glassware twice with 0.1N NaOH.

Transfer this rinse into Container No. 4. (DO NOT RINSE or brush the glass-fritted filter support.) Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to clearly identify its contents.

6.2.5 Blanks. Save a portion of the 0.1N NaOH used for cleanup as a blank. Take 200 mL of this solution directly from the wash bottle being used and place it in a plastic sample container labeled "NaOH blank." Also save samples of the water, and place it in a container labeled "H<sub>2</sub>O blank."

### 6.3 Arsenic Sample Preparation

6.3.1 Container No. 1 (Filter). Place the filter and loose particulate matter in a 150-mL beaker. Also, add the filtered material from Container No. 2 (see Section 6.3.3). Add 50 mL of 0.1N NaOH, then stir and warm on a hot plate at low heat (do not boil) for about 15 minutes. Add 10 mL of concentrated HNO<sub>3</sub>, bring to a boil, then simmer for about 15 minutes. Filter the solution through a glass fiber filter. Wash with hot water, and catch the filtrate in a clean 150-mL beaker. Boil the filtrate and evaporate to dryness. Cool, add 5 mL of 50 percent HNO<sub>3</sub>, and then warm and stir. Allow to cool. Transfer to a 50-mL volumetric flask, dilute to volume with water, and mix well.

### 6.3.2 Container No. 4 (Arsenic Impinger Sample)

NOTE: Prior to analysis, check the liquid level in Containers No. 2 and No. 4: If leakage has occurred during transport, record this on the analysis sheet. If a noticeable amount of leakage occurred, either discard the sample or take steps, subject to approval by the Executive Officer, to adjust the final results.

Transfer the contents of Container No. 4 to a 500-mL volumetric flask, and dilute to 500mL with water. Pipet 50 mL of the solution into a 150-mL beaker. Add 10 mL of concentrated HNO<sub>3</sub>, bring to a boil, and evaporate to dryness. Allow to cool, add 5 mL of 50 percent HNO<sub>3</sub>, and then warm and stir. Allow the solution to cool, transfer to a 50-mL volumetric flask, dilute to volume with water, and mix well.

### 6.3.3 Container No. 2 (Probe Wash). See note in 6.3.2 above. Filter (using a glass fiber filter) the contents of Container No. 2 into a 200-mL volumetric flask. Combine the filtered material with the contents of Container No. 1 (Filter).

Dilute the filtrate to 200 mL with water. Then pipet 50 mL into a 150-mL beaker. Add 10 mL of concentrated HNO<sub>3</sub>, bring to a boil, and evaporate to dryness. Allow to cool, add 5 mL of 50 percent HNO<sub>3</sub>, and then warm and stir. Allow the solution to cool, transfer to a 50-mL volumetric flask, dilute to volume with volume with water, and mix well.

### 6.3.4 Filter Blank. Determine a filter blank using two filters from each lot of filters used in the sampling. Cut each filter into strips, and treat each filter individually as directed in Section 6.3.1 beginning with the sentence, "Add 50 mL of 0.1N NaOH."

### 6.3.5 0.1N NaOH and Water Blanks. Treat separately 50 mL of 0.1 N NaOH and 50 mL water as directed under Section 6.3.2 beginning with the sentence, "Pipet 50 mL of the solution into a 150-mL beaker."

## 6.4 Spectrophotometer Preparation.

Turn on the power, set the wavelength, slit width, and lamp current, and adjust the background corrector as instructed by the manufacturer's manual for the particular atomic absorption spectrophotometer. Adjust the burner and flame characteristics as necessary.

## 6.5 Analysis

6.5.1 Arsenic Determination. Prepare standard solutions as directed under Section 7.1, and measure their absorbances against 0.8 N HNO<sub>3</sub>. Then, determine the absorbances of the filter blank and each sample using 0.8 N HNO<sub>3</sub>, as a reference. If the sample concentration falls outside the range of the calibration curve, make an appropriate dilution with 0.8 N HNO<sub>3</sub>, so that the final concentration falls within the range of the curve. Determine the arsenic concentration in the filter blank (i.e., the average of the two blank values from each lot). Next, using the appropriate standard curve, determine the arsenic concentration in each sample fraction.

6.5.1.1 Arsenic Determination at Low Concentration. The lower limit of flame atomic absorption spectrophotometry is 10 ug As/mL. If the arsenic concentration of any sample is lower than this, use the vapor generator or graphite furnace which is available as an accessory component. The analyst also has the option of using either of these accessories for samples with concentrations between 10 and 30 ug/mL. Follow the manufacturer's instructions in the use of such equipment.

6.5.1.1.1 Vapor Generator Procedure. Place a sample containing between 0 and 5 ug of arsenic in the reaction tube, and dilute to 15 mL with water. Since there is some trial and error involved in this procedure, it may be necessary to screen the samples by conventional atomic absorption until an approximate concentration is determined. After determining the approximate concentration, adjust the volume of the sample accordingly. Pipet 15 mL of concentrated HCl into each tube. Add 1 mL of 30 percent KI solution. Place the reaction tube into a 50°C water bath for 5 minutes. Cool to room temperature. Connect the reaction tube to the vapor generator assembly. When the instrument response has returned to baseline, inject 5.0 mL of 5 percent NaBH<sub>4</sub> and integrate the resulting spectrophotometer signal over a 30-second time period.

6.5.1.1.2 Graphite Furnace Procedure. Dilute the digested sample so that a 5 mL aliquot contains less than 1.5 ug of arsenic. Pipet 5 mL of this digested solution into a 10-mL volumetric flask. Add 1 mL

of the 1 percent nickel nitrate solution, 0.5 mL of 50 percent HNO<sub>3</sub>, and 1 mL of the 3 percent hydrogen peroxide and dilute to 10 mL with water. The sample is now ready for injection into the furnace for analysis. Because of the variation in the instruments of different manufacturers, no detailed operating instructions will be given here. Instead the analyst should follow the instructions provided with his particular instrument.

6.5.1.2 **Mandatory Check for Matrix Effects on the Arsenic Results.** Since the analysis for arsenic by atomic absorption is sensitive to the chemical composition and to the physical properties (viscosity, pH) of the sample (matrix effects), check (mandatory) at least one sample from each source using the "Method of Additions" to ascertain that the chemical composition and physical properties of the sample did not cause erroneous analytical results. Three acceptable "Method of Additions" procedures are described in the General Procedure Section of the Perkin Elmer Corporation Manual (see Reference 10.2). If the results of the Method of Additions procedure on the source sample do not agree within 5 percent of the value of obtained by the routine atomic absorption analysis, then reanalyze all samples from the source using the Method of Additions procedure.

6.5.2 **Container No. 3 (Silica Gel).** The tester may conduct this step in the field. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g; record this weight.

## 6.6 Audit Analysis

Concurrently analyze the two unknown audit samples with each set of compliance samples to evaluate the techniques of the analyst and the standards preparation. (Note: It is recommended that known quality control samples be analyzed prior to the compliance and audit sample analysis to optimize the system's accuracy and precision. One source of these samples is the Source Branch listed in Section 5.3.16).

The same analysis, analytical reagents, and analytical system shall be used both for each set or sets of compliance samples and the EPA audit samples. If this condition is met, audit samples need not be included with any additional compliance analyses performed within the succeeding 30-day period for the same enforcement agency. An audit sample set may

not be used to validate different sets of compliance samples under the jurisdiction of different enforcement agencies unless prior arrangements are made with both enforcement agencies.

Calculate the concentration, in  $\text{g/m}^3$  using the specified sample volume in the audit instructions. (Note: The analyst may determine immediately whether the analyses of the audit samples were acceptable by reporting the audit results in  $\text{g/m}^3$  and compliance results in  $\text{ug/mL}$  by telephone.)

Include the results of both audit samples, their identification numbers and the analysts' names with the results of the compliance determination samples in appropriate reports to the EPA regional office or the appropriate enforcement agency.

Include this information with subsequent compliance analyses for the same enforcement agency during the succeeding 30-day period.

## 7. CALIBRATION

Maintain a laboratory log of all calibrations.

### 7.1 Standard Solutions.

For the high level procedure pipet 1, 3, 5, 8, and 10 mL of the 1.0 mg As/mL stock solution into separate 100-mL volumetric flasks, each containing 1 mL of concentrated  $\text{HNO}_3$ .

If the low-level vapor generator procedure is used, pipet 1, 2, 3, and 5 mL of 1.0  $\text{ug As/mL}$  standard solution into the separate reaction tubes.

For the low level graphite furnace procedure, pipet, 1, 5, 10 and 15 mL of 1.0  $\text{ug As/mL}$  standard solution into the separate flasks along with 2 mL of the 5 percent nickel nitrate solution and 10 mL of the 3 percent hydrogen peroxide solution. Dilute to the mark with water, then treat the standards in the same manner as the samples (Section 6.5).

Check these absorbances frequently against 0.8 N  $\text{HNO}_3$ , (reagent blank) during the analysis to insure that base-line drift has not occurred. Prepare a standard curve of absorbance versus concentration. (Note: For instruments equipped with direct concentration readout devices, preparation of a standard curve will not be necessary.) In all cases, follow calibration and operational procedures in the manufacturer's instruction manual.

## 7.2 Sampling Train Calibration

Calibrate the sampling train components according to the indicated Sections of CARB Method 5: Probe Nozzle (Section 5.1). Pitot Tube Assembly (Section 3.2). Metering System (Section 5.3), Probe Heater (Section 5.4), Temperature Guages (Section 5.5), Leak Check of Metering System (Section 5.6), and Barometer (Section 5.7).

## 8. CALCULATIONS

### 8.1 Nomenclature

$B_{ws}$	=	Water in the gas stream, proportion by volume
$C_a$	=	Concentration of arsenic as read from the standard curve, ug/mL
$C_c$	=	Actual audit concentration, g/m <sup>3</sup>
$C_d$	=	Determined audit concentration, g/m <sup>3</sup>
$C_s$	=	Arsenic concentration in stack gas, dry basis, converted to standard conditions, g/dscm (g/dscf)
$E_a$	=	Arsenic mass emission rate, g/hr
$F_d$	=	Dilution factor (equals 1 if the sample has not been diluted)
$I$	=	percent of isokinetic sampling
$m_{bi}$	=	Total mass of all six impingers and contents before sampling, g
$m_{fi}$	=	Total mass of all six impingers and contents after sampling, g
$m_n$	=	Total mass of arsenic collected in a specific part of the sampling train, ug
$M_t$	=	Total mass of arsenic collected in the sampling train, ug
$T_m$	=	Absolute average dry gas meter temperature (see Figure 423-2), °K (°R)
$V_m$	=	Volume of gas sample as measured by the dry gas meter, dcm (dcf)
$V_{m(std)}$	=	Volume of gas sample as measured by the dry gas meter correlated to standard conditions, scm (scf)
$V_n$	=	Volume of solution in which the arsenic is contained, mL
$V_{w(std)}$	=	Volume of water vapor collected in the sampling train corrected to standard conditions, scm (scf)
$H$	=	Average pressure differential across the orifice meter (see Figure 423-2), mm H <sub>2</sub> O (in. H <sub>2</sub> O)

8.2 Average dry gas meter temperatures ( $T_m$ ) and average orifice pressure drop ( $H$ ). See data sheet (Figure 423-2).



### 8.3 Dry Gas Volume

Using data from this test, calculate  $V_{m(\text{std})}$  by using Eq. 5-1 of CARB Method 5. If necessary, adjust the volume for leakages.

### 8.4 Volume of Water Vapor

$$V_{w(\text{std})} = K_1 (m_{fi} - m_{bi}) \quad \text{Eq. 423-1}$$

Where:

$$\begin{aligned} K_1 &= 0.001334 \text{ m}^3/\text{g} \text{ for metric units} \\ &= 0.047012 \text{ ft}^3/\text{g} \text{ for English units.} \end{aligned}$$

### 8.5 Moisture Content

$$B_{ws} = \frac{V_{w(\text{std})}}{V_{m(\text{std})} + V_{w(\text{std})}} \quad \text{Eq. 423-2}$$

### 8.6 Amount of Arsenic Collected.

8.6.1 Calculate the amount of arsenic collected in each part of sampling train as follows:

$$m_n = C_a F_d V_n \quad \text{Eq. 423-3}$$

8.6.2 Calculate the total amount of arsenic in the sampling train as follows:

$$m_t = m_n(\text{filters}) + m_n(\text{probe}) + m_n(\text{impingers}) - m_n(\text{filter blank}) - m_n(\text{NaOH}) - m_n(\text{H}_2\text{O}) \quad \text{Eq. 423-4}$$

8.7 Calculate the arsenic concentration in the stack (dry basis, adjusted to standard conditions) as follows:

$$C_s = K_2 \left( \frac{m_t}{V_{m(\text{std})}} \right) \quad \text{Eq. 423-5}$$

Where:

$$K_2 = 10^{-6} \text{ g}/\mu\text{g}$$

8.8 Pollutant Mass Rate.

Calculate the arsenic mass emission rate using the following equation.

$$E_a = C_s Q_{sd}$$

Eq. 423-6

The volumetric flow rate,  $Q_{sd}$  should be calculated as indicated in CARB Method 2.

8.9 Isokinetic Variation.

Using data from this test calculate I. Use Eq. 5-8 of Method 5.

8.10 Acceptable Results.

Same as Method 5, Section 6.12

8.11 Relative Error (RE) for QA Audits, Percent.

$$RE = (C_d - C_c) \frac{100}{C_c}$$

Eq. 423-7

9. ALTERNATIVE TEST METHODS FOR INORGANIC ARSENIC

Simultaneous Determination of Particulate and Arsenic Emissions.

The tester may use Method 5 to simultaneously determine As provided that

- 1) he uses acetone to remove particulate from the probe and inside of the filter holder as specified by Method 5,
- 2) he uses a glass fiber filter with a low As background, and
- 3) he treats and analyzes the entire train contents, including the impingers, for As as described in Section 6 of this Method.

10. BIBLIOGRAPHY

10.1 Same as Citations 1 through 9 of Section 7 of Method 5.

10.2 Perkin Elmer Corporation. Analytical Methods for Atomic Absorption Spectrophotometry. 303-0152. Norwalk, Connecticut. September 1976 pp. 5-6.

- 10.3 Standard Specification for Reagent Water. In: Annual Book of ASTM Standards. Part 31; Water, Atmospheric Analysis. American Society for Testing and Materials. Philadelphia PA, 1974 pp. 40-42.
- 10.4 EPA Method 108. Determination of Particulate and Gaseous Arsenic Emissions. 51FR 28035 (August 4, 1986).
- 10.5 U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., Method 7061. Arsenic (Atomic Absorption, Gaseous Hydride). In "Test Methods for Evaluating Solid Waste – Physical/Chemical Methods" SW-846 (1982).