

ARSENIC IN PETROLEUM NAPHTHAS

UOP Method 296-82

SCOPE

This method is for determining total arsenic in petroleum naphthas. The limit of detection for a 500-g naphtha sample is approximately 0.5 μg , which corresponds to one part per billion (1 ppb).

OUTLINE OF METHOD

The arsenic is extracted from the naphtha in 2 steps, using 5% sodium hypochlorite solution and 70% sulfuric acid, respectively. The combined extracts are digested with nitric acid and hydrogen peroxide to destroy organic matter. The resulting sulfuric acid solution containing the arsenic is diluted and transferred to an arsine generator. Zinc is added and the arsine produced is first passed through a tube containing lead acetate to remove hydrogen sulfide and sulfur dioxide. The arsine then comes in contact with a strip of paper which has been impregnated with mercuric bromide. The length of the orange-brown coloration produced on the strip is compared with standards, which have been run under identical conditions.

APPARATUS

Arsenic test strips, 2.5-mm wide and 90-mm long, for impregnation with mercuric bromide (see *Mercuric bromide paper*), Sargent-Welch Scientific Co., Cat. No. S-1095, or equivalent

Balance, capable of weighing to 0.1 mg

Balance, top-loading, capable of weighing to 0.01 g, Mettler PC 2000, Sargent-Welch Scientific Co., Cat. No. S-2556-39, or equivalent

Bath, constant temperature, control from 0 to 100 C within ± 0.2 C, inside dimensions 45 by 31 by 18-cm deep, Blue M Electric Co., Cat. No. MR-3220A-1, or equivalent

Boiling chips, carborundum, Arthur H. Thomas Co., Cat. No. 1590-D30, or equivalent

Bottle, narrow mouth, round, amber glass, 960-mL capacity, Sargent-Welch Scientific Co., Cat. No. S-8245-F, or equivalent

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

Bottle, dropping, 30-mL capacity for stannous chloride

Cylinders, graduated, 10-, 100-, 250- and 1000-mL

Dark cabinet, of sufficient size to enclose the water bath

Flask, Erlenmeyer, 125-mL

Flask, filtering, with side arm, 500-mL

Flask, Kjeldahl, 300-mL, Sargent-Welch Scientific Co., Cat. No. S-34405-D, or equivalent

Flasks, volumetric, 100- and 1000-mL

Forceps, small, steel or chrome plate

Funnel, separatory, Squibb with Teflon stopcock, 1000-mL

Glass wool, borosilicate glass

Grinding balls, Spex Industries, Inc., Cat. No. 8004A, or equivalent

Grinding container, Spex Industries, Inc., Cat. No. 8004, or equivalent

Gutzeit apparatus, as shown in Fig. 1, or arsenic apparatus, improved Gutzeit, SGA Scientific Inc., Cat. No. A-5250, or equivalent

Hot plate

Medicine droppers (or automatic pipets), for nitric acid and hydrogen peroxide

Millimeter scale

Mixer-mill, Spex Industries, Inc., Cat. No. 8000, or equivalent

Pipe cleaners

Pipet, volumetric, 10-mL

Pipets, Mohr, one- and 5-mL

Sieve, 8-inch diameter, U.S.A. Series No. 20 including bottom pan, W.S. Tyler, Inc., or equivalent

Spatula, porcelain, Coors No. 3 or 4, or an equivalent small measuring spoon for approximately 5 g of zinc

Stoppers, rubber, size 00 and 5

Test tube and stopper, for containing immersed mercuric bromide strips

REAGENTS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified. References to water mean deionized or distilled water.

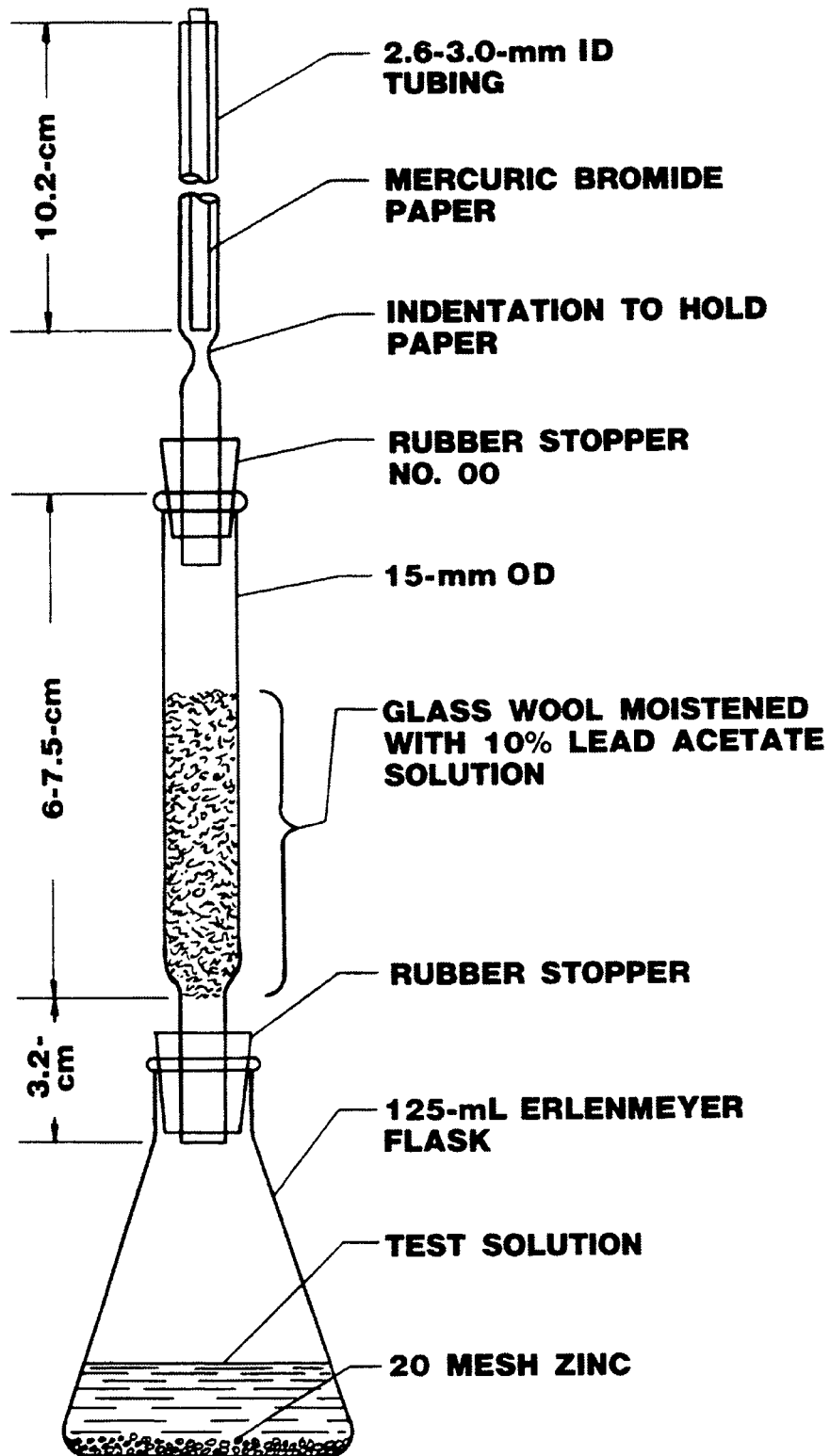


Figure 1

Apparatus for Determination of Arsenic

Acetone

Ammonium oxalate, saturated solution

Arsenic, standard solution. Dissolve $1.320 \text{ g} \pm 0.1 \text{ mg}$ of pure As_2O_3 in 25 mL of 5-*M* sodium hydroxide. Add 25 mL of 3-*M* (1:5) sulfuric acid. Transfer to a 100-mL volumetric flask and dilute to the mark with water. This solution contains 10 mg of As/mL. Make successive dilutions of this stock solution with distilled water to obtain a solution containing $2 \mu\text{g}$ of As/mL. Prepare this dilute solution from the main stock solution once a week.

Hydrochloric acid, concentrated

Hydrogen peroxide, 30%

Lead acetate, 10% solution. Dissolve 100 g of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ in 400 mL of water to which 30 mL of glacial acetic acid has been added. Transfer to a one-liter volumetric flask and dilute to the mark with water.

Mercuric bromide, 5% solution. Dissolve 5 g of mercuric bromide in 100 mL of 95% ethyl alcohol. Store in a dark bottle. Mercuric chloride may be substituted for mercuric bromide.

Mercuric bromide paper. Immerse the arsenic test strips in the mercuric bromide solution for a minimum of 30 minutes. A supply of paper strips may be left in the mercuric bromide in the dark indefinitely and removed as needed. Shortly before use, remove the desired number of strips, blot off excess solution between clean paper towels or filter papers and air dry. Handle the strips with forceps at the opposite end from which the color will be produced.

Nitric acid, concentrated, 0.01-ppm arsenic or less, ACS Reagent Grade, Sargent-Welch Scientific Co., Cat. No. SC13766-001 PT, or equivalent

Potassium iodide. Dissolve 15 g of potassium iodide in 100 mL of water. Store in a brown bottle. Discard any solution over 2 days old.

Sodium hypochlorite (NaOCl), 5% neutral solution, arsenic-free

Stannous chloride. Dissolve 25 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 25 mL of concentrated hydrochloric acid. When the solution is clear, dilute to 100 mL with water.

Sulfuric acid, 70%, diluted from concentrated acid, 0.01-ppm arsenic or less, Reagent Grade, Sargent-Welch Scientific Co., Cat. No. SC15120-001PT, or equivalent. Add cautiously, with stirring, 3 volumes of 95% sulfuric acid to 2 volumes of water.

2,2,4-Trimethylpentane, (isooctane), ACS Reagent Grade, Sargent-Welch Scientific Co., Cat. No. SC15530-001 PT, or equivalent

Zinc, granular, 20-mesh, 0.1-ppm arsenic or less, Sargent-Welch Scientific Co., Cat. No. SC15851-001LB, or equivalent. The zinc commonly contains particles which have air entrapped in them during manufacture causing severe problems in the analysis. Therefore, the commercial granular zinc must be compacted with a Spex mixer-mill and then screened prior to use. Fill the grinding container approximately 1/2 full with zinc and add two grinding balls. Close the mixer and compact for 5 minutes. Remove the compacted zinc from the container and screen through a No. 20 sieve. Discard any zinc that does not pass through the sieve. Collect the zinc passing through the No. 20 sieve and "pickle" it as follows:

Pour 454 g of the zinc into a 600-mL beaker and cover with water to a depth of 2.5 cm. Add 15 mL of concentrated hydrochloric acid. Stir until the surface of the zinc becomes uniformly bright. Pour off the acid, then wash the zinc by decantation and stirring with water until free of acid. Store the zinc under water. It is good practice to leave the porcelain measuring spatula in the beaker to prevent contamination. Cover the beaker with a watch glass.

PROCEDURE

Sampling

Samples must not be stored in the light in clear bottles prior to analysis, since arsenic can be lost to the container walls. Collect samples in amber glass bottles. If these are not available wrap clear bottles in dark paper or otherwise protect from exposure to light. Samples should be analyzed as quickly as possible to minimize losses.

When samples have been stored longer than two weeks, remove the sample from the bottle and determine the arsenic content as described under *Extraction*. In addition, rinse the bottle with sodium hypochlorite and sulfuric acid as described under *Extraction*. Following this, rinse the bottle with 15 mL of a 1:1 solution of nitric acid, previously warmed to 60 C. Carry the rinsings through the digestion and arsine generation, determine the amount of arsenic present and add this quantity to the amount determined in the sample.

Extraction

The optimum quantity of sample taken for analysis should contain less than 12 μg (30 ppb) of arsenic. Typically, a sample weight of 500 g (about 650 mL) is analyzed. Smaller weights may be used if insufficient sample is available but will give a correspondingly higher limit of detection. Samples containing higher levels of arsenic must be diluted with isooctane to reduce the arsenic content to this level. If this is required, a weighed amount of sample is diluted with isooctane to produce a final weight of 500 g.

Place the sample weighed to the nearest 0.01 g, in a 1000-mL separatory funnel. Add 15 mL of 5% sodium hypochlorite solution and shake the sample vigorously for 5 minutes. Allow the layers to separate and transfer the sodium hypochlorite layer to a 300-mL Kjeldahl flask. Extract the sample a second time with 15 mL of 70% sulfuric acid, shaking for 5 minutes, and combine this extract with the sodium hypochlorite extract. Finally, wash the sample with 10 mL of water and combine the wash water with the previous extracts. Rinse the stem of the funnel after each extraction by adding a few milliliters of water without shaking. Combine these washes with the main extracts in the Kjeldahl flask.

Digestion

Add approximately 15-25 mL of concentrated nitric acid to the Kjeldahl flask and swirl the contents of the flask to mix thoroughly. Add 2 or 3 carborundum boiling chips and allow the mixture to stand at room temperature at least 30 minutes, or until any initial reaction has ceased. Warm the contents on a hot plate at approximately 250 C in an efficient hood to start the digestion. (CAUTION: Wear safety goggles and use a safety shield during the oxidation process.)

After the initial evolution of nitric oxide slows down, increase the temperature of the hot plate to approximately 500 C, raising the temperature slowly to avoid excessive foaming. If the oxidation becomes too rapid and foaming occurs through the neck of the Kjeldahl flask, the foam may usually be broken and losses prevented by inserting a cold glass rod into the foam. Foaming generally may be prevented by cautious addition of reagents.

Continue the digestion until practically all the nitric acid is gone, that is, when boiling has stopped and the brown fumes of nitrogen oxides are no longer apparent. The temperature during this nitric acid digestion should be such that gentle reflux occurs but not so high that the nitric acid boils out before most of the oxidation has occurred.

Cautiously add more nitric acid in 2- to 5-mL portions dropwise if there is any evidence of darkening. Repeat the addition of nitric acid as above until there is no further evidence of brown fumes. Allow most of the remaining nitric acid present to distill out. It is *very important* that nitric acid be present in excess during oxidation or loss of arsenic will occur.

Cautiously add 3 to 5 mL of 30% hydrogen peroxide, dropwise, allowing each drop to run down the neck of the inclined flask. Continue adding hydrogen peroxide until fumes of nitrogen oxides are no longer evolved and the solution becomes colorless. This clears the solution temporarily but, on further concentration to evolution of fumes of SO_3 , the solution may again darken. Use either nitric acid or hydrogen peroxide to clear up the solution and again concentrate to fumes. Prior to this fuming, the temperature of the hot plate should be no higher than the 500 C recommended above. Continue this process of heating nearly to fumes of SO_3 and clearing up the solution with either hydrogen peroxide or nitric acid until the solution can be taken to fumes of SO_3 without darkening. A final addition of approximately 5 mL of 30% hydrogen peroxide will ensure the removal of any residual nitric acid.

After oxidation is complete and the solution has been purged of the nitric acid and nitrogen oxides with peroxide, allow the sulfuric acid to concentrate to fumes of SO_3 and reflux in the Kjeldahl flask until beads of sulfuric acid and returning streams of condensing sulfuric acid begin to appear in the neck of the flask. Continue this refluxing of the sulfuric acid for at least 5 minutes. Longer periods will do no harm. No darkening of the sulfuric acid should occur.

If the sulfuric acid darkens again, clear it rapidly by the dropwise addition of hydrogen peroxide. If the darkening persists, it may be necessary to repeat the nitric acid treatment. Follow the nitric acid with sufficient peroxide to remove most of the nitric acid and oxides and again fume for at least 5 minutes with the sulfuric acid refluxing. At this point slowly add 15 mL of saturated ammonium oxalate solution in order to remove the last traces of nitric acid and oxides of nitrogen. Allow the vapors to boil out, then fume for 5 minutes.

Total oxidation and complete removal of nitric acid and oxides of nitrogen are essential to the complete recovery of the arsenic in the ensuing arsine generation. It is also necessary that the solution be kept from more than slight darkening during the digestion in order to avoid possible loss of arsenic.

Generation of Arsine

Allow the contents of the Kjeldahl flask to cool and dilute cautiously with approximately 10 mL of distilled water. Transfer the solution quantitatively to a 125-mL Erlenmeyer flask, using approximately 60 mL of water in three increments for rinsing so that the final volume will be approximately 75 mL. Cool the contents of the flask to room temperature.

Add 5 mL of the potassium iodide solution, swirl and allow the solution to stand for 15 minutes. Then add 1 drop of the stannous chloride solution or more if the iodine is not removed with one drop.

Fit the Erlenmeyer flask with the lead acetate (SO_2 , H_2S removal) guard tube and the small tube containing the mercuric bromide paper (see Fig. 1). To prepare the lead acetate tube, fill the guard tube approximately two-thirds full with firmly packed glass wool. The lower end of the lead acetate guard tube is fitted into a 1-hole rubber stopper placed into the neck of a 500-mL filtering flask connected to a vacuum

line. Wash the glass wool with several portions of water and then 10% lead acetate solution. Add each portion with the vacuum turned off, then draw the liquid through by suction. Blot off any solution remaining on the outside of the guard tube or stopper. The same guard tube may be used repeatedly by washing first with water and then with fresh lead acetate immediately before each use. Clean the mercuric bromide tube with a pipe cleaner. After rinsing with water, rinse with acetone and dry by suction, using the vacuum filtration assembly.

If the temperature of the standard solutions is above ambient after addition of the sulfuric acid, precool the contents of the Erlenmeyer flasks. Then add approximately 5 g of pickled zinc to the standards and sample using a porcelain measuring scoop. This can be conveniently measured with a Coors No. 3 level spatula or a Coors No. 4 heaping spatula. Assemble immediately as shown in Fig. 1. Place the assembled Gutzeit generator in a water bath at room temperature throughout the test. Immerse at least to the neck of the Erlenmeyer flask and preferably to near the top of the lead acetate tube. In addition to temperature control, the immersion permits leaks to be quickly detected and corrected. If the stopper is not immersed, pour water around the outside of the joint to act as a water seal for the detection of leaks. The bottom of the Erlenmeyer flask should be at least 2.5 cm from the bottom of the bath. Allow the reaction to proceed for at least an hour in the dark which may be accomplished by placing a cabinet enclosure over the bath. Maintain constant temperature throughout the reaction period (see Note 1).

Standards

Prepare standards by adding 15 mL of 70% sulfuric acid and the appropriate amount of water to aliquots of the standard arsenic solution to produce standards containing 1, 4 and 12 μg of arsenic. Process these solutions identically to samples, beginning with *Generation of Arsine*. A set of standards should be generated each time samples are analyzed.

Blank Test

Place 15 mL of 70% sulfuric acid in the 300-mL Kjeldahl flask, add 15 mL of 5% sodium hypochlorite solution and 25 mL of concentrated nitric acid and boil to fumes of SO_3 . Add 20 mL of 30% hydrogen peroxide dropwise to the solution. Evaporate to fumes of SO_3 and reflux the sulfuric acid for approximately 5 minutes. Slowly add 15 mL of saturated ammonium oxalate and allow the vapors to boil off. Fume for 5 minutes. Determine the arsenic in the resulting sulfuric acid solution as described under *Generation of Arsine* and *CALCULATIONS*. In general, the blank should be zero or less than 0.5 μg . If values for blanks are greater than 0.5 μg obtain reagents containing lower arsenic levels. Run a new blank each week and each time any one of the reagents is changed. If isooctane is required for dilution, a blank with a corresponding weight should be extracted and analyzed for arsenic.

The Erlenmeyer flasks used for arsine generation should be cleaned by filling them with a dichromate-sulfuric acid cleaning solution for at least an hour after each use. Rinse with at least 4 portions of tap water and 3 portions of distilled water.

CALCULATIONS

In some instances, the generated arsine will form a coloration on the mercuric bromide paper which is brown at the end of the strip but graduates into yellow at the upper portion of the stain. Mark each side of the strip at the point to which it is estimated the brown color would have extended if the coloration had been uniform. In the case of a brown coloration with a yellow edge, this will probably be a point approximately one-third of the distance from the end of the brown color to the end of the yellow color. Measure the total length of the estimated uniform stain as indicated in the paragraph below. For light yellow stains, take the

full stain length, unless the stain is noticeably longer along one edge than the other edge, on the same side of the strip, in which case make a visual estimation or the average of stain lengths to give the correct stain length. Differences between analysts in judging the length of the stains do not affect the results, providing that each analyst uses his own calibration curve.

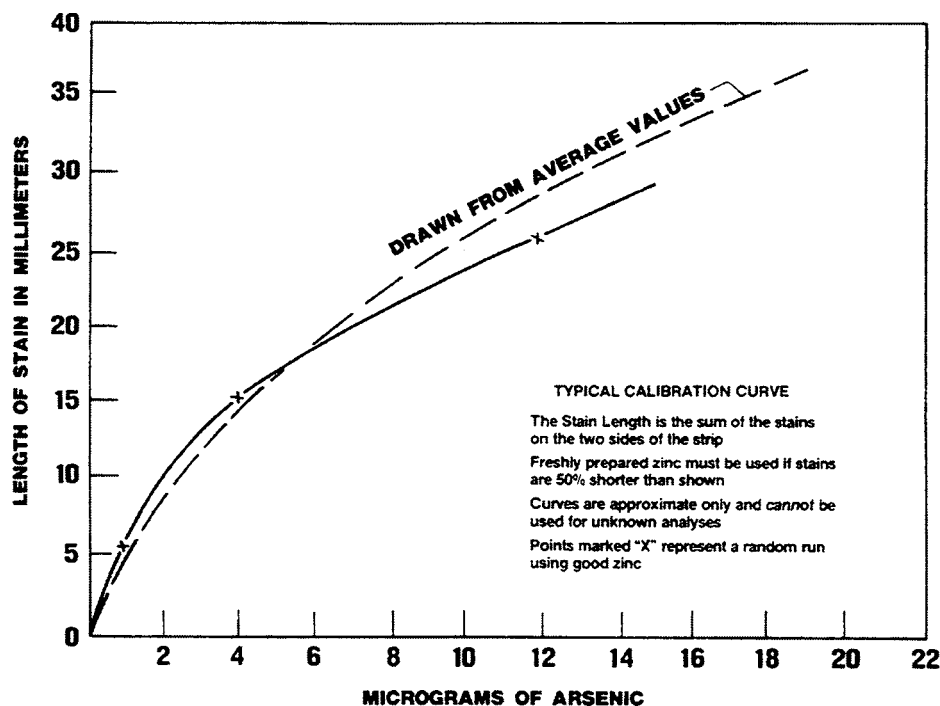


Figure 2

Typical Calibration Curve for Determination of Arsenic

To prepare a calibration curve, measure the length of the stain on each side of the strip, estimating to the nearest 0.1 mm, and add the figures for both sides. Plot these total stain lengths against the number of micrograms of arsenic contained in the standards. A typical calibration curve is shown in Fig. 2. Determine the number of micrograms of arsenic in samples by obtaining the sum of the stain lengths on both sides of the sample strip and reading the result from the prepared calibration curve.

Calculate the arsenic content of the sample in mass parts per billion from the equation:

$$\text{Arsenic, mass-ppb} = \frac{1000 M}{W}$$

where:

M = mass of arsenic obtained from calibration curve, μg

W = mass of sample taken for analysis, g

NOTES AND PRECAUTIONS

1. The intensity and length of the colored stain depend on the rate of evolution of the arsine and the concentration of mercuric bromide in the paper. Too rapid evolution of the arsine will result in a longer, weaker color. An abnormally slow evolution of arsine will give an intensely brown and much shorter stain. It is, therefore, important to maintain as uniform a rate of arsine evolution as possible. This depends on the amount and concentration of acid, the amount and surface area of the zinc and the temperature of the reaction.

2. In the event that inferior quality zinc must be used, the addition of 5 drops of 10% $\text{Cd}(\text{NO}_3)_2$ solution following the addition of the potassium iodide and stannous chloride will result in longer stains.

PRECISION

Based on 6 replicate determinations the estimated standard deviation (esd) for arsenic at the 3.4 ppb level was calculated to be 0.5 ppb.

Duplicate results by the same operator should not differ by more than 1.8 ppb (95% probability) at the stated level.

TIME FOR ANALYSIS

The elapsed time for one analysis is 8 hours. The labor requirement is 1.8 hours.

REFERENCES

Official and Tentative Methods of Analysis, 5th Ed., 390-393, Association of Official Agricultural Chemists, Washington, D.C. (1940).

Scott's Standard Methods of Analysis, 5th Ed., 101-108, D. Van Nostrand, New York (1939).

SUGGESTED SUPPLIERS

Arthur H. Thomas Co., P.O. Box 779, Philadelphia, PA 19105

Blue M Electric Co., Blue Island, IL 60406

Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077

Spex Industries, Inc., Box 798, Metuchen, NJ 08840

SGA Scientific Inc., 770 N. Church Rd., Elmhurst, IL 60126

W. S. Tyler, Inc., 8200 Tyler Blvd., Mentor, OH 44060