

ARSINE IN ETHYLENE BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROPHOTOMETRY

UOP Method 834-82

SCOPE

This method is for determining arsine in ethylene by flameless electrothermal atomic absorption spectrophotometry. Arsine is calculated from the determined arsenic concentration. The lower limit of detection for arsine in ethylene is about 5 ppb.

OUTLINE OF METHOD

A known volume of gas is passed through a tube containing activated charcoal to adsorb the arsine. The charcoal is transferred to bottles and the adsorbed arsine is extracted with 0.1 *M* nitric acid. Nickel nitrate is added to the sample to reduce the volatility of the arsenic and the solutions are analyzed for arsenic by flameless atomic absorption. Peak heights of samples are compared to the peak heights of arsenic standards in a similar matrix. The arsine concentration in the gas is then calculated.

APPARATUS

Atomic absorption spectrophotometer, having a direct readout (or recorder output) proportional to absorbance units, graphite furnace accessory and background corrector accessory. The Perkin Elmer 603 with Model 2200 HGA is one example. An automatic sampler is also helpful but is not necessary. If an automatic sampling system is not used then an Eppendorff automatic pipeter, 20- μ L capacity, Sargent-Welch Scientific Co., Cat. No. S-69721-DS, with plastic disposable tips, Sargent-Welch Scientific, Co., Cat. No. S-69722-AA, or equivalent, must be used.

Balance, capable of weighing 0.1 mg

Balance, top loading, capable of weighing 0.01 g

Bottles, glass, 60-mL, screw cap

Charcoal adsorber tube, glass tubing, 1.1-cm ID by 1.3-cm OD, approximately 20-cm long

Cylinder, graduated, 10-mL

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).

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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Electrodeless discharge lamp, (EDL) arsenic, Perkin-Elmer Corp., Cat. No. 0303-6211, or equivalent

Filter paper, Whatman No. 40, 9-cm diameter, or equivalent

Flasks, volumetric 25-, 100- and 1000-mL, 3 of each required

Funnels, disposable, polypropylene, 55-mm diameter

Gas meter, wet test, 3-liter, Sargent-Welch Scientific Co., Cat. No. S-39466, or equivalent device, for measuring gas flow. A rotometer can be calibrated with the gas to be tested using a wet test meter so that only the rotometer is required during sampling.

Pipets, total volume, one-, 4-, 5-, and 10-mL, three of each required

Power supply, for EDL, Perkin-Elmer Corp., Cat. No. 0057-0761, or equivalent

Regulator, argon, Matheson, Co., Cat. No. 8-580, or equivalent

Stop watch

Ultrasonic cleaner, stainless steel tank, Sargent-Welch Scientific Co., Cat. No. S-82951-B, or equivalent

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit use without reducing the accuracy of the determination. References to water mean deionized.

Argon, 99.995% purity, cylinder, size No. 1 A, 8.21 m³ (290 ft³)

Arsenic trioxide, 99.99% purity, available from Spex Industries, or equivalent

Arsenic stock solution, 1000 µg/mL, standard stock solution may be purchased or prepared as follows: In a 250-mL beaker, dissolve 4 g of sodium hydroxide (NaOH) in 100-mL water. Dissolve 1.3203 g of arsenic trioxide (As₂O₃) in the solution. Acidify this solution with 20 mL of concentrated nitric acid (HNO₃), quantitatively transfer this solution to a one-liter volumetric flask, and fill to the mark with water.

Arsenic working standard, (1) Dilute 10 mL of the 1000 µg/mL arsenic standard solution in a one-liter volumetric flask to one liter with 0.1 M HNO₃ to make a 10 µg/mL standard. (2) Pipet 5 mL of the 10 µg/mL standard into a 100-mL volumetric flask and dilute to volume with 0.1 M HNO₃ to prepare 0.5 µg As/mL. Prepare the 0.5 µg/mL arsenic standard daily.

Charcoal, coconut, activated, 8-12 mesh, available from Sargent-Welch, or equivalent

Glass wool, suitable for filtering

Nickel nitrate hexahydrate, Ni(NO₃)₂·6H₂O, available from J. T. Baker Chemical Co., or equivalent

Nickel nitrate hexahydrate solution, 24.8%. Dissolve 24.780 g of Ni(NO₃)₂·6H₂O in water and dilute to 100 mL

Nitric acid, concentrated

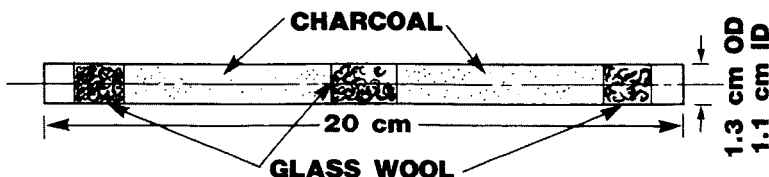
Plastic tubing, Tygon, 12.7-mm ID, Sargent-Welch Scientific Co., Cat. No. S-73650-G, or equivalent

Sodium hydroxide, pellets

PROCEDURE

Arsine Collection

To collect the arsine gas, prepare a charcoal adsorber tube as follows. Pack a 20-cm length of 1.1-cm ID by 1.3-cm OD glass tubing with two 3.0-g sections of charcoal spaced with 1-2 cm of glass wool in the center and glass wool packing on both ends to hold the charcoal in place.



Using short sections of Tygon tubing, connect the charcoal adsorber tube as close to the gas stream source as possible. Place the tube in a vertical position to help avoid channeling of the gas stream through the charcoal. Pass the gas through the tube at a flow rate of 5-6 L/hr until a maximum of 30 liters of gas have been scrubbed. Use a wet test gas meter or equivalent device connected to the exit end of the charcoal tube to accurately measure the flow and gas volume.

Desorption

Clean all glassware with a detergent solution followed by both tap water and deionized water rinses. Then clean the glassware with hot concentrated nitric acid and rinse with deionized water.

To desorb the arsine from the charcoal, transfer the charcoal from the first section (that section which comes in contact with the gas stream first) to a marked 60-mL bottle. Transfer the second section to another marked 60-mL bottle. Also prepare a blank by weighing out 3.0 g of charcoal from the reagent bottle into a third 60-mL bottle. The charcoal used as a blank should be from the same container as the charcoal used in the adsorber tube.

Add 10 mL of 0.1 M HNO_3 to each bottle and cap loosely. Allow released gas to escape for a few minutes to avoid any pressure build up. Tighten caps, shake and place in the bath of an ultrasonic agitator for 30 minutes. Decant the solutions into marked 25-mL volumetric flasks. Repeat two additional times using 8-mL portions of 0.1 M HNO_3 . The charcoal absorbs some of the solution so that the total recovered volume will be about 23 mL. Add one milliliter of 24.8% $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution to each flask. Dilute to volume with 0.1 M HNO_3 and mix. Filter through dry No. 40 Whatman filter paper to remove suspended charcoal fines.

Pipet 10 mL of the 0.5 μg As/mL standard and 4 mL of the nickel nitrate solution into a 100-mL volumetric flask. Dilute to the mark with 0.1 M nitric acid. This standard will contain 0.05 $\mu\text{g}/\text{mL}$ of arsenic and is the standard to which sample peak heights are compared.

Prepare the AAS instrument 30 minutes or more before expected operation to ensure warm up of the EDL and background corrector.

Instrument Parameters

Source	Arsenic EDL
Wavelength	193.7nm
Slit setting	0.7 nm
Background correction	yes
Purge Gas	Argon with 3 sec. gas interrupt
Argon Flow rate	40 mL/minute
Sample size	20 μ L
Graphite tube type	non-coated
Recorder Speed	10 mm/minute
Expansion	2X

Parameters will vary somewhat with different instruments and should be adjusted to produce optimum response.

Graphite Furnace Temperatures

Dry	30 sec	100-130 C
Char	30 sec	1100 C
Atomize	8 sec	2700 C

Duplicate analyses should be set up for each sample that is analyzed. Measure the peak heights of the samples and standard. It is not required to dampen the recorder signal tracing.

CALCULATIONS

Average the peak heights of duplicate injections. Calculate the total μ g of arsenic as follows:

$$As_1 = \frac{A_1 - B}{S} CV$$

If the second section of the charcoal adsorber produces a peak which is higher than the blank, also calculate the following:

$$As_2 = \frac{A_2 - B}{S} CV$$

If As_2 is a positive number then the total arsenic is:

$$As_T, \mu g = As_1 + As_2$$

where:

- A_1 = average peak height of arsenic peaks from first section of charcoal, chart units
- A_2 = average peak height of arsenic peaks from second section of charcoal, chart units
- As_1 = arsenic content of 1st section, μ g
- As_2 = arsenic content of 2nd section, μ g
- As_T = total arsenic content, μ g
- B = average peak height of arsenic peaks from extracted blank, chart units
- C = concentration of arsenic in diluted standard μ g/mL
- S = average peak height of arsenic peaks from standard, chart units
- V = total desorbent volume, mL

After finding total arsenic content, the following equation is used to determine arsine in the gas sample:

$$\text{Arsine, mol-ppb} = \frac{\text{As}_T}{G} (1.333) \frac{24.45}{74.922} \frac{760}{(P)} \frac{(T + 273)}{298} \times 1000$$

where:

G = volume of gas passed through charcoal, L

P = atmospheric pressure at the time of sampling, mm of mercury

T = temperature of gas analyzed C

As_T is as previously defined

1.33 = desorption factor for As in charcoal (75% recovery)

24.45 = molar volume (liter/mole) at 25 C and 760 mm Hg

74.922 = molecular weight of arsenic

298 = standard temperature, K

760 = standard pressure, mm Hg

This expression is reduced to:

$$\text{Arsine, mol-ppb} = \frac{1,110 \text{ As}_T (T + 273)}{GP}$$

PRECISION

Based on 9 replicate determinations, the estimated standard deviation (esd) for arsine at the 5 ppb level was calculated to be 0.89 ppb.

Duplicate results by the same operator should not differ by more than 2.9 ppb (95% probability) at the stated level.

TIME FOR ANALYSIS

The time estimate is based on single sample processing. Total time is dependent on the time required for sampling. If 5 hours are used for sampling, then a single sample can be processed in 7 hours.

The labor requirement may vary but will be about 2-3 hours for a single sample.

SUGGESTED SUPPLIERS

J. T. Baker Chemical Co., 222 Red School Lane, Phillipsburg, NJ 08865

Matheson Co., P.O. Box 96, Joliet, IL 60434

Perkin Elmer Corp., Instrument Div., Main Ave., Norwalk, CT 06856

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

Spex Industries, Inc., P.O. Box 798, Metuchan, NJ 08840