

ARSENIC IN PETROLEUM NAPHTHAS BY HG-AAS

UOP Method 946-96

SCOPE

This method is for determining total arsenic in petroleum naphthas by Hydride Generation-Atomic Absorption Spectroscopy (HG-AAS). The method is quantitative to one mass-ppb (ng/g) when a 100-g sample is used. This method yields results equivalent to, and can be used in place of, UOP Method 296. The method was validated by spiking with triphenylarsine, $\text{As}(\text{C}_6\text{H}_5)_3$; for which 100% recovery was obtained at the 80 mass-ppb level.

OUTLINE OF METHOD

The arsenic is extracted from the naphtha in two steps, using 5% sodium hypochlorite solution and then 70% sulfuric acid. The combined extracts are digested with nitric acid and hydrogen peroxide to destroy organic matter. An aliquot of the resulting sulfuric acid solution containing the arsenic is diluted and reduced with potassium iodide. The diluted and reduced solution is analyzed by HG-AAS to determine the arsenic content.

APPARATUS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, readability 0.1-mg

Balance, top-loading, readability 0.01-g

Beaker, 250-mL, borosilicate glass, Fisher Scientific, Cat. No. 02-540K

Cylinders, graduated, 25-, 100-, 250- and 1000-mL, Fisher Scientific, Cat. Nos. 08-554C, E, F and H, respectively

Flask, Kjeldahl, 300-mL, Pyrex brand, Fisher Scientific, Cat. No. 10-110D

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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Flasks, volumetric, Class A, 50-, 100- and 1000-mL, Fisher Scientific, Cat. Nos. 10-210-5B, 5C and 5G, respectively

Funnel, separatory, Squibb with Teflon stopcock, 500-mL, Kimax brand, Fisher Scientific, Cat. No. 10-437-10D

Heater, transformer-controlled, wire coil, Fisher Scientific, Cat. No. 11-427

Pipets, Mohr, 1- and 5-mL, Kimax brand, Fisher Scientific, Cat. Nos. 13-664D and F, respectively

Pipets, volumetric, Class A, 5- and 10-mL, Fisher Scientific, Cat. Nos. 13-651-1E and 1K, respectively

Spectrophotometer, atomic absorption, having hydride generation capability. A Perkin-Elmer Model 4100 ZL, equipped with a FIAS 400 flow injection analysis system and AS90 autosampler, was used in developing this procedure.

Temperature indicator, noncontact, infrared measuring, Fisher Scientific, Cat. No. 13-904-60

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, unless otherwise specified. References to water mean deionized or distilled water, except where noted.

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Ammonium oxalate, saturated solution, ACS, Alfa Aesar, Cat. No. 36228

Arsenic, standard solution, 0.5 $\mu\text{g/mL}$ (mass/vol-ppm). Pipet 5 mL of 10- $\mu\text{g/mL}$ arsenic standard solution into a 100-mL volumetric flask. Fill to the mark with water, cap and invert several times to thoroughly mix the contents. Discard after each use.

Arsenic, standard solution, 10 $\mu\text{g/mL}$ (mass/vol-ppm). Pipet 10 mL of 1000- $\mu\text{g/mL}$ arsenic stock solution into a one-liter volumetric flask. Dilute to the mark with water. Cap and invert several times to mix thoroughly. Discard after one week.

Arsenic, stock solution, 1000 $\mu\text{g/mL}$ (mass/vol-ppm), SPEX CertiPrep, Cat. No. PLAS2-2X

Boiling chips, carborundum, Fisher Scientific, Cat. No. 09-191-12

Bottles, amber, 237-mL (8-oz), Fisher Scientific, Cat. No. 03-320-4C

Hydrochloric acid, 10% (by volume). Carefully mix one portion of concentrated hydrochloric acid with nine portions of water.

Hydrochloric acid, concentrated, 37%, Certified ACS, Fisher Scientific, Cat. No. A144-212

Hydrogen peroxide, 30%

Lamp, EDL, arsenic, Perkin-Elmer, Cat. No. N305-0605. An arsenic HCL lamp may be substituted if an instrument is used that cannot accommodate an EDL, but performance is somewhat diminished due to losses in both intensity and stability (increased noise).

Nitric acid, concentrated, 70%, Baker Ultrex II, J.T. Baker, Cat. No. 6901-05

Nitric acid, dilute (1:1). Add one part concentrated nitric acid, carefully, to one part water and mix thoroughly.

Pipets, polyethylene transfer, standard bulb, disposable, for use with nitric acid and hydrogen peroxide, Fisher Scientific, Cat. No. 13-711-7

Potassium iodide, ACS Grade, Alfa Aesar, Cat. No. 11601

Potassium iodide, stock solution. Dissolve 10 ± 0.1 g of potassium iodide in 100 mL of water. Store in an amber bottle. Discard any solution over two days old and make new.

Sodium borohydride, Aldrich Chemical, Cat. No. 21,346.2

Sodium borohydride reducing solution, 0.4% in 0.05% NaOH. Using a top-loading balance, weigh 4 ± 0.1 g of sodium borohydride and 1 ± 0.05 g of 50% sodium hydroxide into a 250-mL beaker. Add 100 mL of water and quantitatively transfer to a one-liter volumetric flask with water. Fill to the mark with water, cap and invert several times to thoroughly mix. Depending of specific instrument requirements, other concentrations may be preferable (see *Determination of Arsenic by HG-AAS*).

Sodium hydroxide, 5% (by volume). Carefully mix 1 portion of 50% sodium hydroxide with 9 portions of water.

Sodium hydroxide, 50%, Fisher Scientific, Cat. No. SS410-4

Sodium hypochlorite (NaOCl), 5% neutral solution, arsenic-free, Alfa Aesar, Cat. No. 33369

Sulfuric acid, concentrated, Baker Ultrex, J.T. Baker, Cat. No. 6902-05

Sulfuric acid, 65%. Add cautiously, with stirring, three volumes of concentrated sulfuric acid to two volumes of water.

2,2,4-Trimethylpentane (isooctane), Spectranalyzed, 4-L, Fisher Scientific, Cat. No. O300-4

PROCEDURE

Sampling

The glassware used for this procedure is to be cleaned by filling it with warm (about 60°C) 1:1 nitric acid cleaning solution for at least one hour after each use. Rinse with at least four portions of tap water and three portions of deionized or distilled water. Reserve for this use only.

Collect samples in amber glass bottles, as samples must not be stored exposed to light during shipping and storage. Light promotes the loss of arsenic to the container walls. If amber bottles 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 possible analyte losses.

When samples have been stored longer than two weeks, sample from the bottle and determine the arsenic content as described under *Extraction*. If the whole sample is taken, rinse the bottle with sodium hypochlorite solution and sulfuric acid as described under *Extraction*. Use these rinses to perform the sample extraction and proceed with the decomposition and analysis.

If only a fraction of the sample is taken, transfer the excess sample into another nitric acid cleaned amber bottle. Approximate the volume fraction of sample taken; for example, if a liter of sample was received and approximately 130 mL was taken as the sample, approximately 13% of the original sample was used. Rinse the original sample bottle with sodium hypochlorite and sulfuric acid as described under *Extraction*. Decompose and analyze these washings separate from the sample. Multiply the arsenic concentration obtained for the bottle washes by the volume fraction of sample taken, and add this number to the sample arsenic value obtained from the instrument printout. Use this combined value as **M** in *CALCULATIONS* to determine the total arsenic in the original sample.

Extraction

The quantity of sample taken for analysis should contain less than 10 μg of arsenic. Typically, a sample weight of 100 g (about 130 mL) is analyzed. Smaller quantities may be analyzed if insufficient sample is available, but will yield a correspondingly higher limit of quantitation. 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 the final dilution mass of 100 g.

1. Place the sample, weighed to the nearest 0.01 g, into a 500-mL separatory funnel.
2. Add 15 mL of 5% sodium hypochlorite solution to the funnel, cap and shake vigorously for 5 minutes, periodically releasing pressure, carefully, away from the face.
3. Allow the layers to separate and transfer the sodium hypochlorite (lower) layer to a 300-mL Kjeldahl flask. Wash the stem of the funnel into the Kjeldahl flask with 2 mL of water added to the funnel without shaking, draining the water into the Kjeldahl flask.
4. Add 15 mL of 70% sulfuric acid to the sample in the funnel, shake for 5 minutes, periodically releasing pressure carefully as before, and combine this extract with the sodium hypochlorite extract in the Kjeldahl flask. Again wash the stem of the funnel into the Kjeldahl flask with 2 mL of water added to the funnel without shaking, draining the water into the Kjeldahl flask.
5. Add 10 mL of water to the sample in the funnel, shake for 5 minutes, periodically releasing pressure carefully, and combine this extract with the others in the Kjeldahl flask. Wash the stem of the funnel into the Kjeldahl flask with 2 mL of water added to the funnel without shaking, draining as before.

Digestion

Total oxidation and complete removal of nitric acid and oxides of nitrogen are essential to the complete recovery of arsenic. It is also necessary that the solution be kept from more than slight darkening during the digestion to avoid possible loss of arsenic, because carbonization-reduction will counteract the intended oxidation.

1. Add, cautiously, 25 mL of concentrated nitric acid to the Kjeldahl flask and swirl the flask to thoroughly mix the contents.
2. Add 2 or 3 carborundum boiling chips to the flask and allow the mixture to stand at room temperature for at least 30 minutes, or until any initial reaction has subsided.
3. Warm the contents on the heater set at approximately 250°C, in a hood, to start the digestion. *CAUTION:* Wear safety goggles and use a safety shield during the oxidation process.
4. Increase the heater temperature to approximately 500°C, raising the temperature slowly to avoid excessive foaming, after the initial evolution of nitric oxide slows down.
 - If the oxidation becomes too rapid and foaming occurs through the neck of the Kjeldahl flask, the foam can 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.
 - 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.
5. Continue the digestion until practically all the nitric acid is gone, that is, when boiling has stopped and the brown fumes characteristic of nitrogen oxides are no longer present.
6. Add, cautiously, more nitric acid in 2- to 5-mL portions *dropwise* if there is any evidence of darkening due to the presence of unoxidized carbon. Repeat these additions 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.
7. Add, cautiously, 5 mL of hydrogen peroxide, dropwise, allowing each drop to run down the neck of the inclined flask. Continue adding hydrogen peroxide until fumes of nitrogen oxide are no longer evolved and the solution becomes colorless.
8. Allow the sulfuric acid to concentrate to the release of fumes of sulfur trioxide, 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 for at least 5 minutes, longer periods will do no harm.
 - Prior to this fuming, the heater temperature should be no higher than the 500°C recommended above.
 - If the sulfuric acid solution darkens upon concentration, repeat the addition of nitric acid followed by hydrogen peroxide, Steps 6 and 7. Continue this procedure until the concentrated sulfuric acid solution remains clear and colorless (no further darkening occurs), Step 8.
9. Add, cautiously, 5 mL of hydrogen peroxide, dropwise, to ensure that any residual nitric acid has been removed.
10. Remove the flask from the heater and allow to cool for 5 minutes. Add 15 mL of saturated ammonium oxalate, slowly, to remove the last traces of nitric acid and oxides of nitrogen. Place the flask on the heater, bring the sample to a boil and allow the vapors to boil out, then fume again for 5 minutes.
11. Transfer the contents of the Kjeldahl flask to a 50-mL volumetric flask, quantitatively, with water. Allow the 50-mL flask to cool to room temperature. Bring to volume with water, cap and invert several times to thoroughly mix the contents.

12. Determine the amount of arsenic present in the resulting sulfuric acid solution of the sample as described under *Sample and Standards Preparation for Hydride (Arsine) Generation, Determination of Arsenic by HG-AAS* and *CALCULATIONS*.

Preparation of Blank Solution

The blank solution should be prepared after the sample digestion, so that the reagent additions to the sample can be properly matched.

1. Place 15 mL of 70% sulfuric acid in a 300-mL Kjeldahl flask, add 15 mL of 5% sodium hypochlorite solution, 25 mL of concentrated nitric acid, two to three boiling chips, and boil to the release of fumes of sulfur trioxide.
 - If additional nitric acid is added to the sample during the sample digestion, then an equal amount of concentrated nitric acid must be added to the blank.
2. Add 10 mL of hydrogen peroxide, dropwise, to the solution, evaporate to fumes of sulfur trioxide, and reflux for at least 5 minutes.
3. Remove the flask from the heater and allow to cool for 5 minutes. Add, slowly, 15 mL of saturated ammonium oxalate solution and place the flask on the heater. Bring the sample to a boil and allow the vapors to boil off. Fume for an additional 5 minutes.
4. Allow the blank solution to cool to room temperature. Carefully add 5 to 10 mL of water to the flask and then transfer quantitatively to a 50-mL volumetric flask. Bring to volume with water, cap and invert several times to thoroughly mix the contents.
5. Reserve the blank solution for use in preparation of the standards.
 - 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. Prepare a new blank each week whenever samples are being run, and each time any one of the reagents is changed.
 - If isooctane is required for sample dilution, a blank of corresponding mass should be extracted and analyzed for arsenic.

Sample and Standards Preparation for Hydride (Arsine) Generation

1. Pipet 5 mL of blank solution (from Step 4, *Preparation of Blank Solution*) to each of three 50-mL volumetric flasks.
2. Pipet 1.5 mL of 0.5- $\mu\text{g}/\text{mL}$ arsenic standard to one of the flasks, and 3.0 mL to a second flask. The third flask is used as the blank.
3. Pipet 5 mL of sample solution (from Step 11, *Digestion*) into a fourth 50-mL volumetric flask.
4. Add 10 mL of concentrated hydrochloric acid, followed by 10 mL of 10% potassium iodide solution, to each of the four flasks. Swirl to mix and let stand for one hour. Then bring to volume with water, cap and invert several times to thoroughly mix the contents.
 - The standards and sample are reduced to As^{+3} and are now ready for hydride generation on a suitably equipped atomic absorption spectrophotometer.
 - Standards prepared in this fashion contain 0, 15 and 30 ng/mL As, respectively.

Determination of Arsenic by HG-AAS

There are many different manufacturers of HG-AAS equipment. Generic instructions cannot be written to cover all of the different instruments. Therefore, consult your instrument manual for instructions on determining the arsenic content of the sample, blank and standards. Modern instruments use the standard data to construct a calibration curve. After the sample is run, the arsenic concentration, as read from the calibration curve, is displayed on the instrument printout. Some general instrument parameters for the Perkin-Elmer 4100 ZL are listed in the Table.

If too large a sample size is taken (no estimate of arsenic concentration was available), and the sample concentration detected by the instrument exceeds the upper standard concentration by more than 10%, the digest solution (from Step 11, under *Digestion*) may be diluted once by no more than one in ten, while maintaining the matrix match by use of the blank solution. If the arsenic determination for this additional dilution then falls within the calibration range, the data are accepted. The equation in *CALCULATIONS* must be modified to include this additional dilution. If the arsenic determination for the additional dilution still exceeds the calibration range, the procedure must be performed again, from the beginning, using a smaller amount of sample diluted in isooctane as noted under *Extraction*.

To liberate the arsenic as arsine for measurement by the spectrophotometer, the sample is treated with borohydride. As the exact concentrations of the reagents can vary based on specific manufacturers' specifications, see the operations manual for the instrument being used to properly prepare the required solutions. For the Perkin-Elmer 4100 ZL used in preparing this procedure, the reagents listed in *REAGENTS AND MATERIALS* and the Table are used.

Table
General Instrument Parameters

Wavelength	193.7 nm
Slit	0.7 nm
Lamp, arsenic	EDL (preferred) or HCL
Integration Time	15 sec
Cell temperature	900°C
Reagents	
Carrier solution	10% (v/v) HCl*
Reducing agent	0.4% NaBH₄ in 0.05% NaOH*

* For use with the Perkin-Elmer 4100 ZL.

CALCULATIONS

If a newer, computerized instrument is used, the calculations are all performed in the computer after the sample mass and dilutions are entered. The computer prints out the final sample concentration. If an older instrument is used, use the equation that follows to calculate the final sample concentration. Report to the nearest mass-ppb below 10 mass-ppb, and to two significant figures at or above 10 mass-ppb.

$$\text{Arsenic, mass-ppb (ng/g)} = \frac{500 M}{W}$$

where:

- M** = mass/vol-ppb of arsenic from instrument printout, ng/mL
- W** = mass of sample taken for analysis, g
- 500** = dilution factor = 50(50/5), mL

where:

- 50** = initial and final dilution volumes, mL
- 5** = aliquot taken from initial dilution, mL

PRECISION

Repeatability

Based on two tests performed by one analyst in a single laboratory on each of four different days (8 tests), a within-laboratory estimated standard deviation (esd) of 1.4 mass-ppb was calculated for arsenic at the 80 mass-ppb level. Two tests performed in one laboratory by the same analyst on different days should not differ by more than 5 mass-ppb at the 80 mass-ppb level (95% probability).

Reproducibility

There is insufficient data available to calculate the reproducibility of the test at this time.

TIME FOR ANALYSIS

For one to two samples, the elapsed time for analysis is six hours, with a labor requirement of approximately four hours per sample. For six to eight samples, the elapsed time is one and one-half days, with a labor requirement of approximately two hours per sample.

REFERENCE

UOP Method 296, "Arsenic in Petroleum Naphthas"

SUGGESTED SUPPLIERS

Aldrich Chemical Co., Inc., 1001 W. St. Paul Ave., Milwaukee, WI 53233 (414-273-3850)
Alfa Aesar, Johnson Matthey Catalog Co., 30 Bond St., Ward Hill, MA 01835-8099 (505-521-6300)
Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300)
J.T. Baker Inc., 222 Red School Lane, Phillipsburg, NJ 08865 (908-859-2151)
Perkin-Elmer Corp., Analytical Instruments, 761 Main St., Norwalk, CT 06859-0012 (203-762-1000)
SPEX CertiPrep, Inc., 203 Norcross Avenue, Metuchen, NJ 08840-1253 (908-549-7144)