



A Honeywell Company

Arsenic in Heavy Petroleum Fractions using Microwave Digestion and Graphite Furnace-AAS

UOP Method 986-08

Scope

This method is for determining total arsenic in heavy hydrocarbons by microwave digestion and graphite furnace atomic absorption spectroscopy (GF-AAS). The lower limit of quantitation for arsenic is 50 ng/g (mass-ppb).

Sample preparation by conventional extraction and digestion, such as that used in UOP Method 946, "Arsenic in Petroleum Naphthas by HG-AAS," is problematic for high-boiling samples as it is possible for arsenic to be volatilized at the extreme sample preparation conditions required for the high boiling samples. Microwave digestion does not require these extreme conditions and also requires less operator attention during sample preparation.

References

UOP Method 946, "Arsenic in Petroleum Naphthas by HG-AAS," www.astm.org

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

The samples, along with a reference material and a blank, are digested in a microwave oven. The combined digests are then analyzed by GF-AAS.

Since the microwave can accommodate only approximately 0.2 g of sample per digestion vessel, this results in a quantitation limit of 150 ng/g. To achieve a better quantitation limit the sample is digested in three vessels and the digests are combined. This results in the stated 50 ng/g limit of quantitation.

Apparatus

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

Balance, readable to 0.1 mg

Cylinder, graduated, 10 mL, VWR, Cat. No. 89000-248

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, VWR, Cat. Nos. 89000-402, -404, and -412, respectively

Microwave, with closed digestion vessels and quartz inserts, Milestone, Ethos EZ

Muffle furnace, capable of heating the quartz digestion vessels to 900°C

Pipets, Mohr, 1- and 5-mL, glass, VWR, Cat. Nos. 89003-452 and -458, respectively

Pipet filler, VWR, Cat. No. 53497-115

Spectrophotometer, atomic absorption, with graphite furnace capability (GF-AAS), PerkinElmer Analyst 800, equipped with a FIAS 400 flow injection analysis system and AS90 autosampler

Wash bottle, for water, VWR, Cat. No. 16210-923

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. References to water mean de-ionized or distilled water, except where noted.

Arsenic, stock solution, 1000-µg/mL SPEX CertiPrep, Cat. No. PLAS2-2X

Arsenic, standard solution, 5.0-µg/mL Pipet 5.0 mL of 1000-µg/mL arsenic stock solution into a 1000-mL volumetric flask and dilute to the mark with water. Cap and invert several times to mix thoroughly. Mark the preparation date on the label; discard after one week.

Arsenic, calibration standard solution, 0.025-µg/mL (25-ng/mL). Pipet 5.0 mL of the 5.0-µg/mL arsenic standard solution into a 1000-mL volumetric flask. Fill to the mark with water, cap and invert several times to thoroughly mix the contents. Make a new calibration standard daily.

Arsenic, calibration standard solution, 0.010-µg/mL (10-ng/mL). Pipet 2.0 mL of the 5.0-µg/mL arsenic standard solution into a 1000-mL volumetric flask. Fill to the mark with water, cap and invert several times to thoroughly mix the contents. Make a new calibration standard daily.

Element Blank oil, Conostan 75, Conostan Division, SCP Science.

Bottles, amber, 250-mL (8-oz), for trace metals analysis, VWR, Cat. No. 15900-138

Hydrogen peroxide, 30%, VWR, Cat. No. EM-HX0635-3

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

Matrix modifier solution, palladium and magnesium nitrate. Prepare the matrix modifier solution: pipet 0.5 mL of palladium nitrate solution (1% Pd), 0.5 mL of 1% magnesium nitrate solution and 1 mL of concentrated nitric acid into a 100-mL volumetric flask, fill to the mark with water and mix by shaking.

Magnesium nitrate solution, 1% Mg. Dilute magnesium nitrate (2% Mg) VWR, Cat. No. RCMIMG20KN-50, 1:1 by volume with water

Palladium nitrate solution, 1% Pd, VWR, Cat. No. RCMMPD10KN-100

Nitric acid, concentrated, 70%, for trace analysis, Ultrex II, Mallinckrodt Baker, Cat. No. 6901

NIST Trace Elements in Fuel Oil (No. 6) Standard 1634C, containing mass-ppb metals: As = 143, Co = 151, Ni = 17.54, Se = 102, V = 28.19 (S ~ 2 mass-%), NIST

Pipets, disposable transfer, graduated, polyethylene, 7-mL capacity, standard bulb, for use with nitric acid and hydrogen peroxide, VWR, Cat. No. 16001-188

Water, distilled or deionized

Procedure

The analyst is expected to be familiar with general laboratory practices, the techniques of microwave digestion and GF-AAS, and the equipment being used.

Detection Limits/Sample Size

It has been determined that about 0.2-0.25 g is the maximum sample size that can be digested per quartz vessel by the described microwave oven; this results in a quantitative detection limit of 150 mass-ppb arsenic. Ordinarily, a lower quantitation limit is required. To achieve a lower detection limit, the same sample is weighed into three quartz digestion vessels and the digests are then combined into the same volumetric flask. This results in a quantitation limit of about 50 ppb arsenic. The blank (element base oil, arsenic free) and the reference (NIST-1634C, 143 ug/g arsenic) are also digested in multi vessels.

Microwave Digestion

Samples are digested in a Milestone Ethos EZ, or equivalent, microwave oven having a capacity of 10 digestion vessels. Prior to each use, the quartz digestion vessel inserts are heated at 600-900°C for about 1 hour to volatilize any arsenic contamination. The blank and the reference are digested in the same manner as the samples.

1. Add 10 mL of distilled water and 2 mL of 30% hydrogen peroxide (H_2O_2) to the digestion vessels; this is to trap digestion fumes.
2. Weigh 0.20-0.25 g of sample to the nearest 0.001 g into the quartz liner (previously heated at 600-900°C and cooled) and insert the quartz liner into the digestion vessel; then add 7 mL of concentrated nitric acid (HNO_3) and 1 mL of hydrogen peroxide (H_2O_2).
3. Close with the supplied tool and place in the microwave. Set up three digestion vessels each per sample, blank and reference.
4. Set the digestion conditions listed in Table 1 and start the oven sequence.
 - Other conditions may be used provides they produce equivalent results.

Table 1
Digestion Conditions

Initial Temperature	ambient
Ramp time	25 minutes
Final Temperature	235°C (~8.6°C/min)
Hold time	40 minutes

5. Allow the digestion vessels to cool to room temperature.
6. Select the replicate digests which are to be combined, open the vessels and quantitatively transfer the digests with water into a 50 mL volumetric flask. Dilute to mark with water and mix well.
7. Dispose of the trap solution according to local safety practices and in an environmentally safe manner.

Graphite Furnace – AAS Determination of Arsenic

The GF-AAS is calibrated with prepared standards using the autosampler. Three calibration points are obtained by analyzing a blank and the 10 and 25 ng/mL arsenic standards. Samples are then analyzed and the 25 ng/mL standard is reanalyzed as a sample at the end of the run. A matrix modifier composed of palladium and magnesium nitrate is used to stabilize the arsenic and permit a higher pyrolysis temperature.

2. Set up the GF-AAS instrument according to the manufacturer's recommended conditions.
 - The default settings in the method are for a 20 uL sample injection and a 5 uL injection of the matrix modifier, which are used without change.
3. Transfer aliquots of the digested sample, blank, and reference into autosampler cups, filling to the level recommended by the instrument manufacturer.
4. Transfer aliquots of the calibration standards and matrix modifier into autosampler cups, filling to the level recommended by the instrument manufacturer.
5. Enter the locations of all the solutions to be analyzed into the instrument data system.
6. Run the blank, calibration standards, the samples, and the reference. At the end of the series, analyze the 25-ng/mL standard as a sample.
 - Analysis of the reference confirms that the system is functioning properly.
 - If the standard run at the end of the series does not repeat within the repeatability allowable difference shown under Precision, check the apparatus and technique, and after fixing any problems found, rerun the samples.
7. Dispose of the remaining solutions according to local safety practices and in an environmentally safe manner.

Calculations

All calculations are performed by the instrument data system after the sample mass and dilutions are entered, and sample results are reported directly in ng/g. If all the data is not entered into the instrument data system, the results will be reported in ng/mL. Use Equation 1 to calculate the final sample concentration.

$$\text{Arsenic, ng/g (mass-ppb)} = \frac{50 S}{T} \quad (1)$$

where:

S = ng/mL arsenic in the analyzed solution as reported by the instrument

T = total mass of the sample weighed into the three vessels, g

50 = diluted volume of the combined digests, mL

Report results in mass-ppb to two significant figures.

Note

This method is strongly recommended for determination of arsenic in heavy hydrocarbons, however, some modifications are possible. In all cases, the NIST Reference must be utilized to ensure reliable results.

1. Hydride Generation-AAS (HG-AAS) can be used if a Graphite Furnace is not available. When using HG-AAS, the sample must be fully digested, thus the microwave digest is taken to fumes as described in UOP Method 946.

2. Microwave digestion can be replaced by extraction and hot plate digestion as described in UOP Method 946.

Recovery and precision have not been determined for these alternatives for arsenic in heavy oils.

Precision

Precision statements were determined using UOP Method 999.

Repeatability and Site Precision

A nested design was carried out for determining arsenic in a sample with two analysts in one laboratory. Each analyst carried out tests on three separate days, performing two tests on the sample each day. The total number of tests was 12. The precision data are summarized in Table 1. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable difference with 95% confidence.

The data in Table 1 are a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Reproducibility

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

Table 1
Repeatability and Site Precision, ng/g (mass-ppb)

<u>Sample</u>	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
NIST Reference 1634C	140	3.7	13	20.4	80

Bias

Analysis of the NIST reference shows no bias from the stated value for arsenic, within the error of the method.

Time for Analysis

The elapsed time for one analysis is approximately 6 hours. The labor requirement is approximately 2.5 hours.

Suggested Suppliers

Conostan Division, SCP Science, 21800 Clark Graham Avenue, Baie D'Urfé, QC, H9X 4B6
Canada (514-457-0701) www.conostan.com

Mallinckrodt Baker, Inc., 222 Red School Lane, Phillipsburg NJ 08865 (908-859-2151)
www.mallbaker.com

Milestone Inc., 25 Controls Dr., Shelton, CT 06484 (866-995-5100) www.milestonesci.com

National Institute of Standards and Technology (NIST), Standard Reference Materials Group, 100
Bureau Dr., Gaithersburg, MD 20899 (301-975-6776) www.nist.gov

PerkinElmer Analytical Instruments, 710 Bridgeport Avenue, Shelton, CT 06484-4794 (203-925-4600) www.perkinelmer.com

SPEX CertiPrep, Inc., 203 Norcross Ave., Metuchen, NJ 08840 (732-549-7144) www.spexcsp.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380 (610-431-1700) www.vwr.com