



A Honeywell Company

Trace Arsenic in Liquid Organics and Heavy Petroleum Fractions by ICP-MS

UOP Method 992-11

Scope

This method is for determining total trace arsenic in liquid organics and heavy petroleum fractions by microwave digestion and Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). The lower limit of quantitation for arsenic is 5 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 time consuming and is problematic for high-boiling samples as it is possible for arsenic to be volatilized at the extreme sample preparation conditions required. UOP Method 986, "Arsenic in Heavy Petroleum Fractions using Microwave Digestion and Graphite Furnace-AAS," uses microwave digestion, however due to sensitivity limitations of the GF-AAS, multiple digestions must be combined for analysis. A comparison of the methods is shown in Table 1.

Table 1
Comparison of Trace Arsenic Methods

<u>Method</u>	<u>Application</u>	<u>Sample Preparation</u>	<u>Analytical Technique</u>	<u>Lower Limit of Quantitation, ng/g</u>	<u>Sample Required, g</u>
946	Petroleum naphthas	Extraction/digestion	Hydride Generation-AAS	80	100
986	Heavy petroleum fractions	Microwave digestion	Graphite Furnace-AAS	50	0.6
992	Liquid organics	Microwave digestion	ICP-MS	5	0.25

References

Operator Manual, UltraCLAVE MA 033, www.milestonesci.com

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

UOP Method 986, "Arsenic in Heavy Petroleum Fractions using Microwave Digestion and Graphite Furnace-AAS" www.astm.org

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 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 digested solutions (digestates) are then analyzed by ICP-MS.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used (see *Procedure*).

Balance, readable to 0.0001 g

Beaker, PTFE, 600-mL, Lab Safety Supply, Cat. No. CQ1-38705

Cylinders, graduated, 10- and 250-mL, polypropylene, VWR, Cat. Nos. 24780-268 and -323, respectively

Flasks, volumetric, polypropylene 25-, 50-, 100-, and 1000-mL, VWR Cat. Nos. 83008-964, 29615-018, 29615-007, and 29615-062, respectively; several of each required

Hot plate, VWR, Cat. No. 12365-378

ICP-MS, PerkinElmer, DRC-e, equipped with an AS10 autosampler

Microwave oven, 15-vessel capacity, with closed digestion vessels, quartz cells and lids, step-up transformer, CryoLab chiller, and computer, Milestone, UltraCLAVE

Oven, drying, capable of operation at 110°C

Pipet, electronic, EDP 3-Plus, SE3-10mL (1–10-mL), Rainin Instrument

Pipet, automatic, 10-100 µL, VWR, Cat. No. 89079-968

Pipet, automatic, 10-1000 µL, VWR, Cat. No. 89079-974

Regulator, argon, two-stage, high-purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-580

Regulator, nitrogen or argon, two-stage, high-purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-580

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

Watch glass, 100-mm diameter, VWR, Cat. No. 66110-087

Water purification system, producing Type 1 water with 18.2 MΩ-cm resistivity, Thermo Scientific Barnstead EASYpure II Ultrapure Water Purification System, Fisher Scientific, Cat. No. 09-050-44

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 passed through a purification system, except where noted.

Argon, 99.995% minimum purity

Element base oil, Conostan 75, Conostan Division, SCP Science

Grease, RS Silicone, Milestone, Cat. No. SP0002

Hydrogen peroxide, 30%, Fisher Scientific, Cat. No. H325-100

Lubricant, dry spray, silicone or PTFE, local supply, or W. W. Grainger, Cat. No. 4JB33

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

Nitric acid, 1-%. Pipet 10 mL of concentrated nitric acid into a 1000-mL volumetric flask containing approximately 500 mL of water. Dilute to volume with water. Cap and invert several times to mix thoroughly.

Nitric acid, 2-%. Pipet 20 mL of concentrated nitric acid into a 1000-mL volumetric flask containing approximately 500 mL of water. Dilute to volume with water. Cap and invert several times to mix thoroughly.

Nitrogen or argon, for microwave, lab gas or cylinder

O-ring, replacement, for UltraCLAVE vessel, Milestone, Cat. Nos. OR0108 (bottom) and OR0107, (top)

Pipet tips, for automatic pipet, 1-200 μL and 100-1250 μL , VWR, Cat. Nos. 53508-810 and -922, respectively

Pipet tips, for electronic pipet, Rainin Instrument, Cat. No. RC-10 mL

Quartz cells and lids, for microwave, 20-mL, Milestone, Cat. No. 39042. If desired, the cells may be marked for identification using an engraver, Dremel, W. W. Grainger, Cat. No. 3XA70

Reference, NIST Trace Elements in Fuel Oil (No. 6) Standard 1634C, containing 143 ng/g (mass-ppb) arsenic, along with other trace elements, NIST. If this specific standard is no longer available or expired, use a currently available similar standard.

Sample tubes, autosampler, centrifuge tubes, 50-mL for standards, 15-mL for samples, VWR, Cat. Nos. 21008-725 and -673, respectively

Standard metal solutions, arsenic(As), gallium(Ga), germanium(Ge), and indium(In), 1000- $\mu\text{g/mL}$, aqueous, SPEX CertiPrep, Cat. Nos. PLAS2-2X, PLGA2-2X, PLGE9-2X, and PLIN2-2X, respectively

Sulfuric acid, concentrated, trace metals grade, VWR, Cat. No. EM-SX1248-6

Water, deionized or distilled, for further treatment in the water purification system

Water, tap

Water purification cartridges, for Barnstead EASYpure II, Type 1 kit, Fisher Scientific, Cat. No. 09-034-167 (for deionized feedwater), or Cat. No. 09-034-168 (for distilled or RO feedwater)

Procedure

The analyst is expected to be familiar with general laboratory practices, the techniques of microwave digestion and ICP-MS, and the equipment being used. This procedure is written for the microwave and ICP-MS listed in *Apparatus*. If different equipment is used, modify the procedure as needed. Dispose of used reagents, materials, and samples in an environmentally safe manner according to local regulations.

Preparation of Stock Solutions

Arsenic, stock solution, 1.0- $\mu\text{g/mL}$

1. Pipet 100 μL of 1000- $\mu\text{g/mL}$ arsenic standard metal solution into a 100-mL volumetric flask containing approximately 50 mL of 1-% nitric acid.

2. Dilute to the mark with 1-% nitric acid. Cap and invert several times to mix thoroughly.
3. Mark the preparation date on the label; discard after one month.

Internal standard stock solution, 2.0- μ g/mL

1. Pipet 200 μ L of each of the 1000- μ g/mL gallium, germanium and indium standard metal solutions into a 100-mL volumetric flask containing approximately 50 mL of 1-% nitric acid.
2. Dilute to the mark with 1 % nitric acid. Cap and invert several times to mix thoroughly.
3. Mark the preparation date on the label; discard after one month.
 - Germanium is used as the internal standard. Gallium and indium are added to stabilize the sample solutions.

Cleaning of Quartz Cells and Lids

Clean the quartz cells and lids as follows:

1. Place quartz cells and lids in a 600-mL beaker, cover with 2-% nitric acid, and place a watch glass on top.
2. Place the beaker on a hot plate. Set the hot plate to 200°C and bring to a boil. Adjust the temperature of the hot plate to maintain a slow boil. Boil for two hours.
3. Remove from the hot plate, and allow to cool.
4. Decant the acid and dispose of it in an environmentally safe manner according to local regulations.
5. Rinse the quartz cells, lids, beaker, and watch glass with water, and place in an oven at 110°C oven for a minimum of one hour to dry.
6. Store the cells and lids in the beaker, covered with the watch glass until needed. For convenience, they may be stored in the oven at 110 °C.

Microwave Digestion

Prior to each use, the pre-cleaned quartz cells and lids are heated at 110°C for about 1 hour and allowed to cool. If they are stored in the oven, they are simply removed and allowed to cool.

The blank (element base oil) and the reference (NIST Standard) are digested in the same manner as the samples.

1. Warm and shake oils and heavier organic liquids to ensure homogeneity.
2. Weigh 0.20-0.25 g, and record the weight of each sample, to the nearest 0.0001 g, into the previously heated and cooled quartz cells. Then, using a graduated cylinder, add 3 mL of concentrated nitric acid (HNO_3) to the quartz cells. Cover with a lid.
3. Weigh 0.20-0.25 g of the reference, to the nearest 0.0001 g, into the previously heated and cooled quartz cells. Then, using a graduated cylinder, add 3 mL of concentrated nitric acid (HNO_3) to the quartz cells. Cover with a lid.
4. Weigh 0.20-0.25 g of the element base oil, which contains no arsenic, to the nearest 0.0001 g, into each of three additional previously heated and cooled quartz cells. Then, using a graduated cylinder, add 3 mL of concentrated nitric acid (HNO_3) to the quartz cells. Cover with a lid.
 - One cell is used for preparing the blank and the other two are used for standard preparation. This is to ensure matrix matching with the samples.

5. Place the covered cells into the sample holder with fixed PTFE cover as described in the UltraCLAVE Operator Manual.
6. Set up the microwave as described below. Refer to the UltraCLAVE Operator Manual for details. Add the load/absorption media as follows:
 - a. Add 400 mL of water, 30 mL of 30% hydrogen peroxide, and 5 mL of sulfuric acid into a PTFE insert that goes into the stainless steel pressure vessel. This acts as absorption media.
 - b. Ensure that all O-rings are properly cleaned and greased.
7. Check the water level in the CryoLab chiller. Add tap water if necessary.
8. Turn on gas (nitrogen or argon), step up transformer, CryoLab chiller, Computer, and UltraCLAVE to rates and settings specified by the manufacturer.
9. Program the system using the settings shown in Table 2.
 - Other conditions may be used provided they produce equivalent results.
10. Load the samples into the UltraCLAVE. Hang sample containers with the fixed PTFE cover as described in the UltraCLAVE Operator Manual.
11. Check the method, parameters, and start the run.
 - At the end of the digestion process, when the materials have cooled, the UltraCLAVE system opens automatically.

Table 2
Digestion Conditions

<u>Nr</u>	<u>t (min)</u>	<u>E (w)</u>	<u>T1°C</u>	<u>T2°C</u>	<u>P</u>
1.	00:40:00	1200	230	80	150
2.	00:40:00	1200	230	80	150

Nr. 1 is for reaching to the prescribed condition,
and Nr. 2 is holding at that condition.

12. Carefully remove the sample holder with the quartz cells.
13. Quantitatively transfer with water the contents of each quartz cell and lid into separate 25-mL volumetric flasks.
14. Into one of the flasks containing the digestate of the element base oil, pipet 250 μ L of the 1.0 μ g/mL arsenic stock solution. Label as calibration standard solution, 10 ng/g.
15. Into a second flask containing the digestate of the element base oil, pipet 500 μ L of the 1.0 μ g/mL arsenic stock solution. Label as calibration standard solution, 20 ng/g.
 - The third flask containing the digestate of the element base oil is the blank.
16. Add 1000 μ L of internal standard to each volumetric flask.
17. Fill to the mark with water, cap and invert several times to thoroughly mix the contents.
18. To avoid corrosion of the UltraCLAVE's stainless steel pressure vessel, immediately after use, carefully clean, dry, and wipe with silicone as described in the UltraCLAVE Operator Manual. Also clean the PTFE container and quartz vessels.

ICP-MS Determination of Arsenic

The ICP-MS is calibrated with prepared standards using the autosampler. Three calibration points are obtained by analyzing a blank and the 10- and 20-ng/mL arsenic standards. Samples are then analyzed.

1. Set up the instrument according to the manufacturer's recommended conditions (see Table 3).

Table 3
ICP-MS Parameters

ICP/MS instrument:	Perkin Elmer DRC-e
Analyte:	⁷⁵ As
Internal standard:	⁶⁹ Ga, ⁷⁴ Ge, ¹¹⁵ In (Ge is used as the internal standard)
RF power	1100 W
Plasma gas flow:	15 L/min
Auxiliary gas flow rate	1.2 L/min
Nebulizer	Nebulizer Cross Flow II
Nebulizer gas flow rate	approximately 0.85 L/min
Spray chamber:	Ryton™ Scott-type
Ion sampling and skimmer cone	Nickel cone
Sampling distance	10 mm from load coil
Sample flush	35 seconds
Read delay	15 seconds
Wash	30 seconds
Peristaltic pump speed	-20 rpm
Resolution:	Standard
Detector mode	Dual
Dwell time	50 ms
Sweeps per reading	20
Readings per replicate	1
Replicates	3

2. Transfer aliquots of the digested samples, blank, reference, and calibration standards into autosampler tubes.
3. Enter the autosampler tray locations of all the solutions to be analyzed into the instrument data system.
4. Run the blank and the 10- and 20-ng/mL arsenic calibration standards and establish the linear calibration curve. Reanalyze the arsenic standards as samples. Analyze the samples and the reference. Reanalyze the arsenic standards as samples at the end of the run.
 - If the standards run as samples do not repeat within 5 % of their values, check the apparatus and technique, and after fixing any problems found, rerun the calibration standards, samples, and reference.
 - Analysis of the reference confirms that the system is functioning properly.
5. Dispose of the remaining solutions in an environmentally safe manner according to local regulations.

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.

$$\text{Arsenic, ng/g} = \frac{25 C}{W} \quad (1)$$

where:

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

W = sample weight, g

25 = diluted volume of the digestate, mL

Report results in ng/g to two significant figures.

Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods," from data obtained using an autosampler.

Repeatability and Site Precision

A nested design was carried out for determining arsenic on three samples, by two analysts, with each analyst performing analyses on two separate days, performing two analyses each day for a total of 24 analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table 4. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 4 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 4 with 95% confidence.

Table 4
Repeatability and Site Precision, Arsenic, ng/g

<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>
A	20.2	0.58	2.3	0.59	2.3
B	49.4	0.94	3.7	0.96	3.8
C	201.2	1.62	6.4	3.54	15.9

The data in Table 4 represent short-term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of long-term repeatability.

Reproducibility

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

Time for Analysis

The elapsed time for one analysis is approximately 5 hours. The labor requirement is approximately 2 hours.

Suggested Suppliers

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

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785, USA (412-490-8300)
www.fishersci.com

Lab Safety Supply, Janesville, WI 53547, USA (608-754-7160) www.lss.com

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

Matheson Tri-Gas, 166 Keystone Dr., Montgomeryville, PA 18936, USA (215-641-2700)
www.mathesontrigas.com

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

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

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

Rainin Instrument Co., Mack Road, Woburn, MA 01801, USA (800-472-4646) www.rainin.com

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

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

W.W. Grainger, Inc., 100 Grainger Parkway, Lake Forest, IL 60045-5201, USA (847-535-1000)
www.grainger.com