

TOTAL MERCURY AND MERCURY SPECIES IN LIQUID HYDROCARBONS

UOP Method 938-00

SCOPE

This method is for determining total mercury in liquid hydrocarbons using a Nippon Instruments Corporation (NIC) Mercury Analyzer. The method may be applied to samples containing 0.1 to 10,000 ng/mL (m/v-ppb). The results can be converted to mass-ppb. The *APPENDIX* contains a procedure, *Determination of Mercury Species in Hydrocarbons*, which can be used to differentiate between elemental mercury, organic non-ionic mercury and ionic (both inorganic and organic) mercury species.

OUTLINE OF METHOD

The NIC Mercury Analyzer/Model SP-3D, consisting of a controller, a mercury atomizer and a mercury detector, is specified for this method. The sample is decomposed by heating in the instrument and the mercury vapor in the gaseous products is collected by the mercury collector as gold amalgam. The temperature of the mercury collector is kept at 150°C to prevent the adsorption of combustion products on the collector. After collection, the amalgam is heated and the mercury is re-amalgamated on a second collector. Upon completion of the two-step gold amalgamation process, the mercury is liberated by heating the collector to 700°C. The vaporized mercury is carried to an absorption cell with a pure carrier gas and detected by the cold vapor atomic absorption technique. After introducing the sample, all operations from the sample decomposition process to the mercury detection and calculation are carried out automatically by the instrument.

APPARATUS

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

Balance, readability 0.1-mg

Crucibles, high-form, 50-mL, Fisher Scientific, Cat. No. 07-965G, several required

Flasks, volumetric, glass, Class A, 100- (three required), 500- and 1000-mL, Fisher Scientific, Cat. Nos. 10-210-8C, F and G, respectively

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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Furnace, muffle, 120 V, 50/60 Hz, 1200°C maximum, Fisher Scientific, Cat. No. 10-554-28

Mercury analyzer, NIC, Model SP-3D (no substitute), with the following accessories:

Air purifier, NIC, Cat. No. 2750-01

Boats, ceramic, NIC, Cat. No. 2744

Collector tube, quartz, Model M 160, NIC, Cat. No. 2704-01

Drawing rod, for boats, NIC, Cat. No. 2725-01

Heat tube, NIC, Cat. No. 2702

Inlet cap for naphtha, NIC, Cat. No. 2710-01N

Joints, 6-mm diameter, NIC, Cat. No. 2715-6

Joints, 8-mm diameter, NIC, Cat. No. 2715-8

Mercury collector, chromosorb coated with gold, NIC, Cat. No. 2751

O-rings, NIC, Cat. No. 2733

Paper, NIC, Cat. No. 2757-02

Printer, NIC, Cat. No. 2606

Sample vessel, for boats and additives, NIC, Model SK-1

Spoon, NIC, Cat. No. 2748-02

Stand, boat, NIC, Cat. No. 2709

Micropipet, V₃ series, variable volume 20-200 µL, Baxter Scientific, Cat. No. P5054-11 (required for the analysis of heavy hydrocarbon and calibration samples)

Pipets, volumetric, Class A, 1-, 2-, 5- and 10-mL, Fisher Scientific, Cat. Nos. 13-660A, B, E and F, respectively

Recorder, 1-V full scale, 1-sec or less full-scale response, optional

Syringe, 100- and 250-µL capacity, Supelco, Cat. Nos. 2-1498M and -0784M, respectively (required for the analysis of light hydrocarbon)

Tweezers, flat, round point, Baxter Scientific, Cat. No. E1200-9

Wash bottle, Nalgene, LDPE, 500-mL, Fisher Scientific, Cat. No. 03-409-17F (used for nitric acid washing of all glassware)

Wash bottle, Nalgene™, Right to Know Safety, 1000-mL, for acetone, Fisher Scientific, Cat. No. 03-409-11F

Wash bottle, Nalgene™, Right to Know Safety, 1000-mL, for water, Fisher Scientific, Cat. No. 03-409-11K

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.

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

Acetone, Fisher Scientific, Cat. No. A18-4

Additive B, NIC, Cat. No. 2754-02

Additive M, prepare by mixing 350 g of calcium hydroxide and 500 g of sodium carbonate. This can be purchased from NIC premixed, Cat. No. 2754-01

Calcium hydroxide, 99.5% purity, Sigma Chemical, Cat. No. C7887

L-Cysteine, 99% purity, Pfaltz and Bauer, Cat. No. C33800

Mercuric chloride, mercury (II) chloride, 99.999% purity, Aldrich Chemical, Cat. No. 20-377-7

Nitric acid, concentrated, Trace Metal Grade, Fisher Scientific, Cat. No. A509-212

Nitric Acid, 1:1. Combine 250 mL of concentrated nitric acid with 250 mL of water in a plastic wash bottle, swirl to mix, and use freshly prepared while still warm.

Phosphate buffer, pH 7.2, Baxter Scientific, Cat. No. H299-1. Some phosphate buffers contain mercury compounds as a preservative. The buffer must be mercury free.

Pipet tips, disposable, Baxter Scientific, Cat. No. P5054-27

Sodium carbonate, 99.99% purity, Aldrich Chemical, Cat. No. 22,442-0

Weighing paper, Fisher Scientific, Cat. No. 09-898-12A

PROCEDURE

All glassware must be thoroughly cleaned by washing with 1:1 nitric acid, rinsed with water, rinsed with acetone, followed by blow-drying with nitrogen or oil-free clean air.

Sampling

Samples should be collected in a manner that assures representative sampling. Elemental mercury and organic-mercury species are unstable and will react with the walls of the sample containers. **Do not collect samples in metal containers. Any mercury present will adsorb on the metal.** Samples should be collected in previously acid cleaned glass containers, approximately 500-mL in size, then analyzed as soon as possible. Samples should be kept refrigerated if stored. If samples must be shipped to another site for analysis, use pressure-tight containers and the speediest form of transport available.

Instrument Set Up

1. Set up the instrument according to the manufacturer's instructions.
2. Turn on the power to the instrument in the order shown below.
 - Step-down transformer
 - AC stabilizer
 - Controller MA-1
 - Detector MD-1
 - Printer
 - Recorder
3. Establish the conditions required for the analysis as indicated in Table 1.

Table 1
Operating Conditions

Temperature of sample heating furnace	950°C
Temperature of decomposition furnace element	850°C
Pre-heating temperature of mercury collector	150°C
Mercury collector temperature	700°C
Carrier gas	Dry purified room air
Carrier gas pressure	0.4 kg/cm² (39 kPa)
Combustion system flow rate	0.5 L/min
Measuring system flow rate (AAS)	0.5 L/min
Recorder chart speed	5 mm/min
Recorder full scale	1 V
Analysis time (dependent on heating mode and measuring range)	5 - 15 min

4. Confirm that the AC stabilizer has power and its output voltage is 100V AC by observing the voltmeter on the AC stabilizer panel.
 - If necessary, adjust to the correct values.
5. Dilute an equal volume of phosphate buffer and distilled water. Pour the dilute buffer into scrubber bottle 1 located on the left position in the cooler.
 - The level of the liquid must be 10 to 20 mm above the air bubble outlet.

6. Turn the leak check switch of the mercury atomizer (MA) upward.
 - The system is now closed.
7. Verify that the gas pressure, the combustion system flow and the measuring system flow correspond to the settings in Table 1.
 - If necessary, adjust the operating conditions to the correct values.
8. Close each of the exhaust outlets, located in the rear lower center of the mercury atomizer by placing your finger over each opening and ensure that there is no leakage by observing the flow rate decrease to zero.
 - Only one exhaust outlet should be closed at a time; do not close both at the same time or excessive pressure will build up in the instrument.
 - If there is a leak, consult the instruction manual for the correct procedure to follow.
9. Turn the leak check switch downward and allow the system to warm up for one hour.
 - The system is now open.

Preparation of *L*-Cysteine Solution and Standards

***L*-Cysteine Solution, Approximately 10-mg/L**

1. Weigh approximately 0.010 g of *L*-cysteine, to the nearest 0.1 mg, onto a weighing paper.
2. Transfer quantitatively with water into a 1000-mL volumetric flask. Pipet 2 mL of concentrated nitric acid and dilute to the mark with water. Cap and invert several times to mix thoroughly.
 - *L*-cysteine prevents the deposition of mercury on the walls of the glassware.

Mercury Standard, Approximately 100-mg/L

1. Weigh approximately 0.067 g of mercuric chloride, to the nearest 0.1 mg, onto a weighing paper.
2. Transfer quantitatively with the 10-mg/L *L*-cysteine solution into a 500-mL (0.5-L) volumetric flask.
3. Dilute to the mark with the 10-mg/mL *L*-cysteine solution. Cap and invert several times to mix thoroughly.
4. Calculate the concentration of mercury (Hg) in the standard to three significant figures as follows:

$$\text{Hg, mg/L} = \frac{10^3 (0.739) M}{0.5} \quad (1)$$

where:

M = mass of mercuric chloride, g

0.5 = dilution volume, L

0.739 = molecular mass of mercury (200.6) divided by the molecular mass of mercuric chloride (271.5)

10³ = factor to convert g to mg

Mercury Standard, Approximately 10-mg/L

1. Pipet 10 mL of the 100-mg/L mercuric chloride standard into a 100-mL volumetric flask.
2. Dilute to volume with the 10-mg/L *L*-cysteine solution. Cap and invert several times to mix thoroughly.
 - The actual concentration of this standard will be one-tenth of the standard being diluted.

Mercury Standard, Approximately 5-mg/L

1. Pipet 5 mL of the 100-mg/L mercury standard into a 100-mL volumetric flask.
2. Dilute to volume with the 10-mg/L *L*-cysteine solution. Cap and invert several times to mix thoroughly.
 - The actual concentration of this standard will be one-twentieth of the standard being diluted.

Mercury Standard, Approximately 1-mg/L

1. Pipet 1 mL of the 100-mg/L mercury standard into a 100-mL volumetric flask.
2. Dilute to volume with the 10-mg/mL *L*-cysteine solution. Cap and invert several times to mix thoroughly.
 - The actual concentration of this standard will be one-hundredth of the standard being diluted.

Mercury Standard, Approximately 0.1-mg/L

1. Pipet 10 mL of the 1-mg/L mercury standard into a 100-mL volumetric flask.
2. Dilute to volume with the 10-mg/L *L*-cysteine solution. Cap and invert several times to mix thoroughly.
 - The actual concentration of this standard will be one-tenth of the standard being diluted.

Mercury Standard, Approximately 0.01-mg/L

1. Pipet 10 mL of the 0.1-mg/L mercury standard into a 100-mL volumetric flask.
2. Dilute to volume with the 10-mg/L *L*-cysteine solution. Cap and invert several times to mix thoroughly.
 - The actual concentration of this standard will be one-tenth of the standard being diluted.

The mercury standard solutions should be stored in a cool dark place. The maximum shelf life of the solutions is as follows:

10-mg/L *L*-cysteine solution - 6 months

Mercury standard solutions with concentrations 0.1 mg/L and greater - 6 months

Analysis of Light Hydrocarbons

Samples that contain volatile material, e.g., gasoline, are analyzed using this procedure. Less volatile hydrocarbons, e.g., kerosene, diesel, and heavier, are analyzed using the heavy hydrocarbons procedure.

Preparation of Additives and Sample Boats

Heat-treated portions of Additive B should be used for each analysis.

1. Set the muffle furnace temperature at $700 \pm 50^{\circ}\text{C}$.
2. Place approximately 30 g of Additive B into crucibles and place them in the muffle furnace.
 - If the sample is known to contain sulfur compounds, it may be appropriate to use Additive M in addition to Additive B. Consult the instrument manufacturer for current information and procedures.
3. Place sample boats to be used for the analysis in the muffle furnace.
 - Normally two boats are used for the analysis.
4. Heat boats and the additive for at least 2 hours.

Preparation and Measurement of Blank

1. Remove the crucible containing Additive B and the boats from the furnace and place them inside the sample vessel.
 - The boats and additives are kept in the sample vessel to prevent contamination by mercury in the air.
2. Set the MA-1 controller to Mode 2 and select a measuring range. Table 2 serves as a guide for selecting a measuring range. The selection of the range depends on the expected mercury content of the sample.

Table 2
Calibration Ranges and Standards

<u>Measuring Range, ng</u>	<u>Standard Solution, mg/L</u>	<u>Standard Solution Injection Volume, μL</u>
2	0.01	50, 100, 150
20	0.1	50, 100, 150
200	1	50, 100, 150
1000	5	50, 100, 150

3. Press “START” to perform an analysis without inserting a sample boat into the combustion tube of the analyzer.
 - This is to expel any mercury gas remaining in the analyzer.
 - The buzzer will sound when the measurement is completed.

4. Remove the sample boats from the sample vessel. Spread approximately 3 g of Additive B into the boats as shown in Fig. 3.
 - Tweezers must be used when handling the boats.
5. Store one of the boats inside the sample vessel.
6. Open the inlet cover, insert the other boat into the combustion tube and use the drawing rod to position the boat to the mark indicated on the rod. Close the inlet cover.
 - This will position the boat at the hottest point in the furnace.
7. Press “MENU” and select “1” to access the calibration program. Select option “2” for calibration curve “Y=A+Blank.” Enter zero in the console program (panel of MD-1) for the amount of mercury in the blank.
8. Press “START” to begin the analysis.
 - This will be the blank measurement.
9. Remove the boat from the combustion tube after the analysis is completed and place it in the sample vessel.
10. Repeat Steps 6 through 8 using the other boat containing Additive B.

Calibration

It is recommended the analyzer be calibrated once a week, during times when samples are being analyzed. To create the calibration curve, the measurement of three mercury standards is recommended. Use Table 2 to select the appropriate range, standard solution and injection volumes. For example, if a sample is known to contain approximately 1 ng mercury per 100 μ L sample (~10 ppb mercury), use the 2 ng range and the 0.01 mg/L mercury standard (this will be used as a stock standard). Using the 0.01 mg/L mercury standard, analyze calibration samples with 50-, 100- and 150- μ L additions of the standard as shown in Table 2 and according to the following procedure.

1. Open the inlet cover.
2. Remove the sample boat from the combustion tube of the analyzer using the drawing rod and store it in the sample vessel. Immediately remove the other boat containing Additive B from the sample vessel and place it on the boat stand.
3. Add, by micropipet, the appropriate volume of the mercury standard solution on top of Additive
 - This will be the first calibration sample.
 - Table 2 serves as a guide to determine the volumes to be added.
4. Insert the sample boat into the combustion tube, and use the drawing rod to position the boat to the mark indicated on the rod.
 - This will position the boat at the hottest point in the furnace.

5. Close the inlet cover. Press “START” to begin the analysis and enter the amount of mercury in the standard sample in the console program (panel of MD-1).
 - When the analysis is completed, the boat in use should be placed inside the sample vessel to cool.
 - The boat and additive are reusable.
 - While the boat from Step 4 is cooling, the boat in the sample vessel should be used for the next analysis.
6. Repeat Steps 1 through 5 for the second and third calibration samples. Alternate the use of the two boats between calibration samples.
7. Press “MENU” to exit the calibration program after the analysis of all the calibration samples is completed.
 - Upon completion of the analysis of the calibration samples, the analyzer will display the slope of the calibration curve and the correlation coefficient.
 - If the slope of the calibration is less than 0.7 or greater than 1.3, or the correlation coefficient is less than 0.95, consult the instruction manual for corrective action.
8. Remove the sample boat, containing the third calibration sample, from the combustion tube and store it in the sample vessel.

Sample Analysis

1. Remove a cooled sample boat from the sample vessel and place it at the entrance of the combustion tube as shown in Fig. 1. Inject, by syringe, 100 μ L of the sample into the bottom of the sample boat that contains Additive B, as shown in Fig. 1.
 - Unfamiliar samples should be screened at the 1000 ng scale.
 - If the sample is known to contain sulfur compounds, it may be appropriate to use Additive M in addition to Additive B. Consult the instrument manufacturer for current information and procedures.
2. Push the boat into the inlet of the combustion tube as shown in Fig. 2 and close the tube with the inlet cap for naphtha.
 - This cap has a built in push-rod; the push-rod is fully withdrawn in this step.
3. Set the analyzer to Mode 4 and press “START”. Enter the volume of the sample in the console program.
4. Allow the system to remain as is for exactly five minutes.
 - This is to allow samples containing light material to vaporize slowly.
5. When the instrument signals the end of the five minute evaporation time, push the sample all the way into the combustion furnace with the push rod, withdraw the rod, and push “START” again.
6. Remove the boat after the analysis is completed and place it in the sample vessel. Begin the next measurement using the other boat.
7. Repeat Steps 2 through 7 until all samples are analyzed.
 - It is a good practice to analyze a standard as a sample in the beginning and at the end of the analysis of a set of samples to ensure that the equipment is functioning properly. However, if the number of samples is large, the reference sample should be run more often.
 - Occasional duplicate analyses may be performed in order to increase confidence in the results.

Analysis of Heavy Hydrocarbons

Preparation of Additives and Sample Boats

Heat-treated portions of Additives B and M should be used for each analysis.

1. Set the muffle furnace at $700 \pm 50^{\circ}\text{C}$.
2. Place approximately 30 g each of Additives B and M into separate crucibles (at least two pairs) and place them in the muffle furnace.
3. Place sample boats, to be used in the analysis, in the muffle furnace.
 - Normally two boats are used for the analysis.
4. Heat boats and additives for at least 2 hours.

Preparation and Measurement of the Blank

1. Set the MA-1 controller to Mode 3 and select a measuring range.
 - Table 2 serves as a guide to select a range. The selection of range depends on the expected mercury content of the sample.
2. Perform the analysis without inserting a sample boat into the furnace of the analyzer by pressing “START”.
 - This is to expel any mercury gas remaining in the analyzer.
 - The buzzer will sound when the analysis is completed.
3. Remove one boat from the sample vessel and spread approximately 2 g of Additive B and approximately 3.5 g of Additive M into the boat in the order shown in Fig. 3.
 - Tweezers should be used when handling the boats.
4. Open the inlet cover. Insert the boat containing Additives B and M into the combustion tube and use the drawing rod to position the boat to the mark indicated on the drawing rod. Close the inlet cover.
5. Press “MENU” and select “1” to access the calibration program. Select option “2” for calibration curve “Y=A+Blank.” Enter zero in the console program for the amount of mercury in the blank.
6. Press “START” to measure the blank level of mercury in the additives.
 - These additives can only be used for one analysis. After completion, the additives should be discarded in compliance with regulatory guidance.
 - The boat is re-usable.
7. Place the two crucibles from Step 2 into the muffle furnace and remove from the furnace another pair of crucibles that contain Additives B and M. Place the crucibles in the sample vessel and allow them to cool.
 - Step 7 should take place as soon as the analysis in Step 6 has begun.
 - The time required to cool the Additives B and M is usually one measurement cycle. For example, the additives in Step 7 can be used when the measurement in Step 6 is completed.

8. Remove the sample boat from the combustion tube when the analysis is completed, discard the additives and store the boat in the sample vessel.
 - The use of boats should be alternated between analyses.

Calibration

It is recommended that the analyzer be calibrated once a week, during times when samples are being analyzed. To create the calibration curve, the measurement of three mercury standards is recommended. Use Table 2 to select the appropriate range, standard solution and injection volumes. For example, if a sample is known to contain approximately 1 ng mercury per 100 μ L of sample (~10 ppb mercury), use the 2 ng range and the 0.01 mg/L mercury standard (this will be used as a stock standard). Using the 0.01 mg/L mercury standard, analyze calibration samples consisting of 50-, 100- and 150- μ L additions of the standard as shown in Table 2 and according to the following procedure.

1. Remove a boat from the sample vessel. Spread approximately 1 g of Additive B in the boat and add the mercury standard solution, by micropipet, on top of Additive B (see Fig. 4). Cover the standard with additional Additive B, approximately 1 g, and follow with approximately 3.5 g of Additive M (see Fig. 5).
 - The appropriate volume of the mercury standard solution that should be used is listed in Table 2.
2. Open the inlet cover and insert the sample boat in the combustion tube to the position specified on the drawing rod. Close the inlet cover.
3. Press “START” to begin the analysis and enter the amount of mercury in the standard sample in the console program (panel of MD-1).
4. Remove the sample boat from the combustion tube after completion of the analysis and discard the additives. Store the boat in the sample vessel.
 - The additives can only be used for one analysis, although the boats are reusable.
 - The use of the two boats should be alternated between analyses.
 - During each analysis, the crucibles containing Additives B and M should be placed in the muffle furnace while the two crucibles already in the muffle furnace should be taken out and placed in the sample vessel to cool. Use the additives from these crucibles to perform the next calibration step.
5. Repeat Steps 1 through 4 for the second and third calibration samples using heat treated portions of Additives B and M for each analysis.
6. Press “MENU” to exit the calibration program after the analysis of all the calibration samples is completed.
 - Upon completion of the analysis of the calibration samples, the analyzer will display the slope of the calibration curve and the correlation coefficient.
 - If the slope of the calibration is less than 0.7 or greater than 1.3 or the correlation coefficient is less than 0.95, consult the instruction manual for corrective action.

Sample Analysis

1. Remove a boat from the sample vessel and place it on the boat stand. Spread 1 g of Additive B on the bottom of the sample boat. Place boat and boat stand on the balance and tare.

2. Add, by micropipet or dropper, less than 0.1 g of the sample and weigh to the nearest 0.1 mg. Record the weight.
 - The procedure is shown in Fig. 4.
3. Remove the sample boat from the balance. Cover the sample soaked in Additive B with an additional 1 g of Additive B and 3.5 g of Additive M in the order shown in Fig. 5.
4. Remove the inlet cover and place the sample boat into the combustion tube to the position marked on the drawing rod. Immediately close the combustion tube with the inlet cover.
5. Press “START” to begin the analysis. Enter the sample weight into the console program.
6. Remove the boat after the analysis is completed and discard the additives. Place the boat in the sample vessel.
7. Repeat Steps 1 through 6 until all samples are analyzed.
 - It is a good practice to analyze a standard as a sample in the beginning and at the end of the analysis of a set of samples to ensure that the equipment is functioning properly. However, if the number of samples is large, the reference sample should be run more often.
 - Occasional duplicate analyses may be performed in order to increase confidence in the results.

CALCULATIONS

All calculations are performed by the microprocessor, printed out automatically and results are reported to 3 significant figures. Volatile samples run by Mode 4 are reported as ng/mL (m/v-ppb) or mg/mL (m/v-ppm). The results can be converted to mass-ppb or mass-ppm by dividing by the sample density, which can be determined by ASTM Method D 4052 or other means. The results for heavy hydrocarbons are calculated as ng/g (mass-ppb) or $\mu\text{g/g}$ (mass-ppm).

PRECISION

Repeatability

Based on two tests performed by each of two analysts, on each of two days (8 tests) in one laboratory, the within-laboratory estimated standard deviations (esd) were calculated for mercury at the concentrations listed in Table 3. Two tests performed in the one laboratory by different analysts on different days should not differ by more than the allowable difference values listed in Table 3 at the concentrations listed. This data was prepared using UOP Method 888.

Table 3
Repeatability

Mercury Concentration, ng/mL	Within-Lab esd, ng/mL	Allowable Difference (95% Probability) ng/mL
0.8	0.05	0.2
47	0.8	3

Reproducibility

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

TIME FOR ANALYSIS

The elapsed time for one analysis including calibration is 1.3 hours. The labor requirement is 1.3 hours.

REFERENCE

ASTM Method D 4052, *1999 Annual Book of ASTM Standards*, **05.02**, ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19248-2959 (610-832-9500)

UOP Method 888, "Precision Statements in UOP Methods"

SUGGESTED SUPPLIERS

Aldrich Chemical Co., Inc., P.O. Box 355, Milwaukee, WI 53201 (414-273-3850)
 Baxter Scientific Products, 1430 Waukegan Rd., McGaw Park, IL 60085-6787 (708-689-8410)
 Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300)
 Nippon Instruments Corp., 14-8 Akaoji-cho, Takatsuki-shi, Osaka, 569 Japan (0726 94-5195) (Fax 0726-94-0663)
 Pfaltz and Bauer, 172 E. Aurora St., Waterbury, CT 06708 (203-574-0075)
 Sigma Chemical Co., 3050 Spruce St., St. Louis, MO 63103 (314-771-5765)
 Supelco, Inc., Supelco Park, Bellefonte, PA 16823 (814-359-3441)

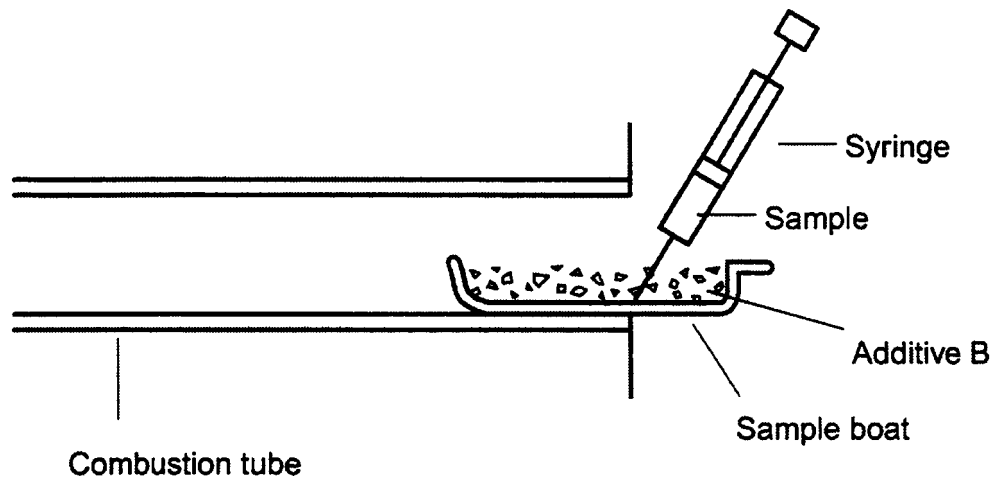


Figure 1

Boat with Additive B for Light Hydrocarbon Analysis

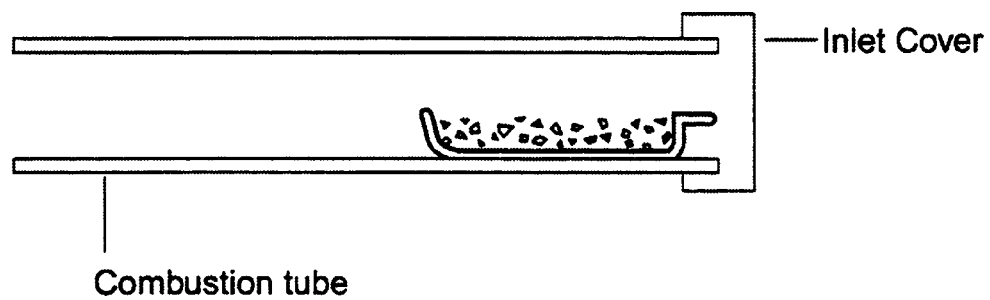


Figure 2

Boat with Additive B and Sample for Light Hydrocarbon Analysis - Initial Position

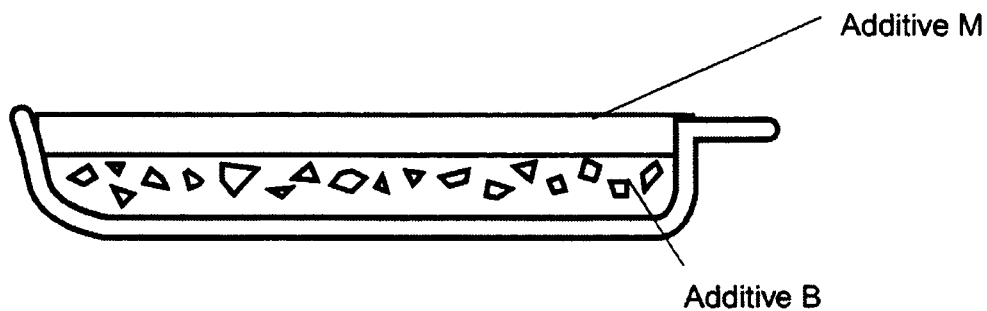


Figure 3

Boat with Additives B and M
for the Analysis of a Blank
for Heavy Hydrocarbon Analysis

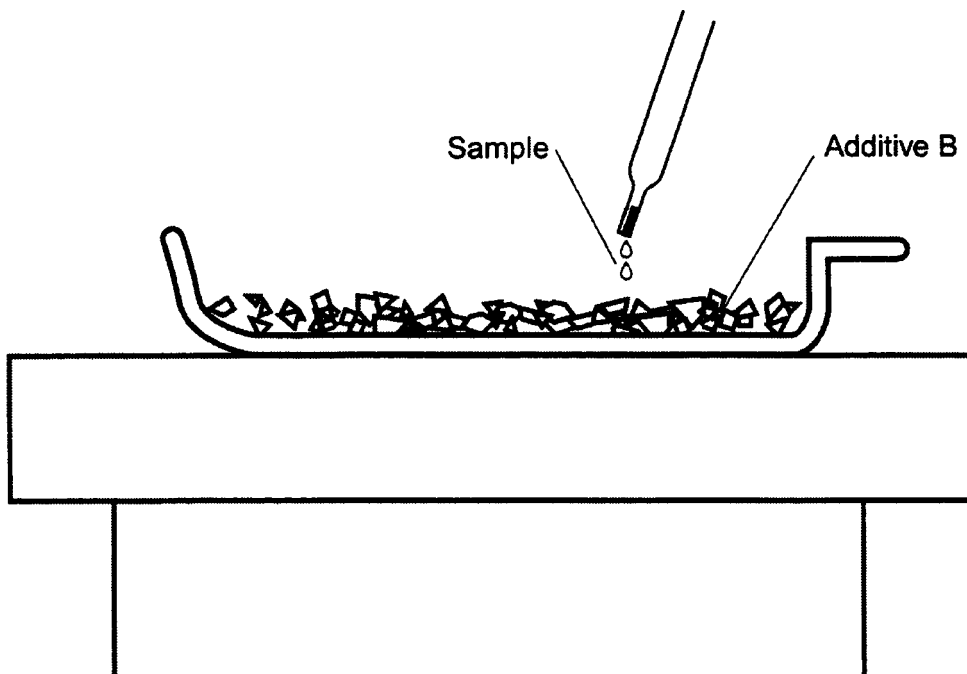


Figure 4

Boat with Additive B and Sample
for Heavy Hydrocarbon Analysis

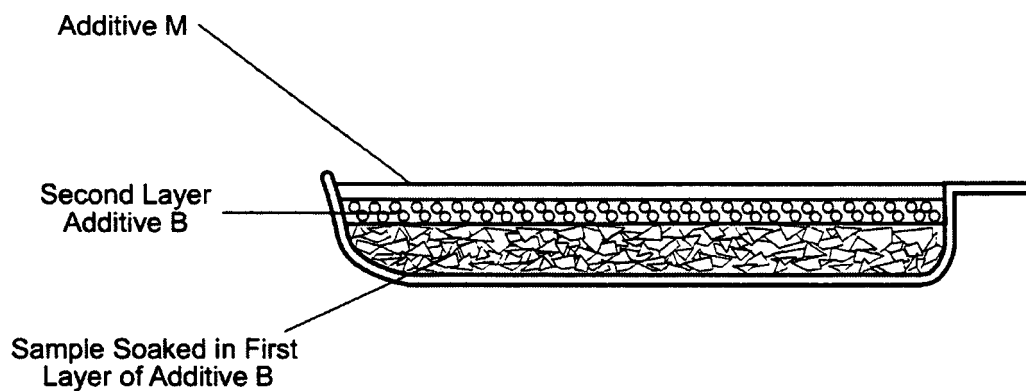


Figure 5

Boat with Additive B and M and
Sample for Heavy Hydrocarbon Analysis

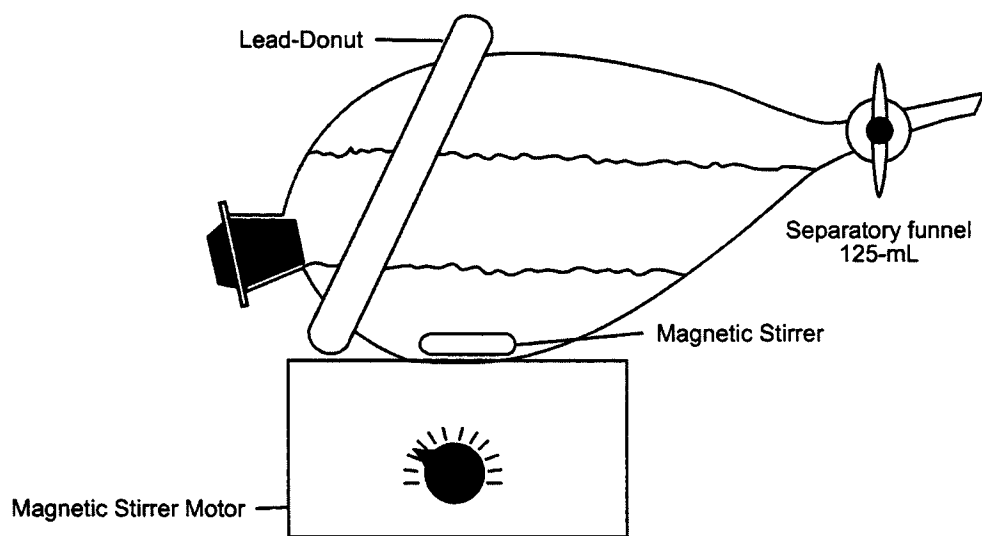


Figure A-1

Separatory Funnel Positioning
for Organic/Aqueous Bi-Phase Sample Extraction

APPENDIX

DETERMINATION OF MERCURY SPECIES IN HYDROCARBONS

SCOPE

This appendix is for the separation and determination of soluble mercury species in hydrocarbons: elemental mercury, organic non-ionic mercury compounds and ionic (both inorganic and organic) mercury compounds. This procedure has been applied to samples containing 15 to 4000 ng/mL (m/v-ppb) of soluble mercury. This procedure is adapted from Furuta, A., Sato, K. and Takahashi, K., *Trace Analysis of Mercury Compounds in Natural Gas Condensate*. Some dimethylmercury will be measured as elemental mercury due to its volatility.

OUTLINE OF METHOD

Any insoluble materials are first removed by pressure filtration. The particulate free hydrocarbon sample is first analyzed for total soluble mercury content. It is then placed in an ice bath and purged with helium. The difference in the original and purged sample mercury concentrations represents the elemental mercury content (see Note 2). The purged sample is then extracted with a 1% *L*-cysteine solution to transfer the ionic species into an aqueous phase. The remaining purged, aqueous-extracted hydrocarbon sample is now analyzed for organic mercury.

APPARATUS

The following items are required in addition to the apparatus listed in the main method.

References to catalog numbers are included as a convenience to the method user. Other suppliers may be used, unless stated otherwise.

Bottles, clear Boston rounds, Qorpak, Poly-Seal™ lined closures, 60- and 473-mL, Fisher Scientific, Cat. Nos. 03-326-5B and -5E, respectively

Dish, crystallizing, Kimax™, 170-x 90-mm, Fisher Scientific, Cat. Nos. 08-762-10 (used for the ice-bath for the purging procedure)

Cylinder, graduated, Pyrex™, Class A, 50-mL, Fisher Scientific, Cat. No. 08-553-A

Flask, volumetric, glass, Class A, 1000-mL, Fisher Scientific, Cat. No. 10-210-G

Flowmeter, digital, range to 700-mL/min, Model 520, Fisher Scientific, Cat. No. 11-164-45

Funnel, short stem, 75-mm top diameter, Fisher Scientific, Cat. No. 10-322E

Gas washing bottle, 250-mL, Pyrex, with fritted disk, coarse porosity, Fisher Scientific, Cat. No. 03-038B

Lead donut, a PVC-coated stabilizer weight, inside diameter approximately 5-cm, 650-g weight, I²R-Inc., Cat. No. LD-5C

Magnetic stirrer, Fisher Scientific, Cat. No. 11-500-49S

Magnetic stir bars, TFE starburst stirring heads, 19-mm diameter, Fisher Scientific, Cat. No. 14-511-96B (must fit inside separatory funnel)

Pipets, volumetric, Class A, borosilicate glass, 15-, 20-, 25-, 30- and 50-mL, Fisher Scientific, Cat. Nos. 13-260-2M, -2N, -2P, -2Q and -2S, respectively

Pressure filtration apparatus, consisting of:

Filters, 0.22-micron, 25-mm diameter, polyvinylidene fluoride, Durapore membrane, hydrophobic, Millipore, Cat. No. GVHP 025-00

Filter holder, Swinny-Stainless Steel, with Luer-Lok, 25-mm, Millipore, Cat. No. XX30-025-00

Forceps, for Millipore filters, Millipore, Cat. No. XX62-000-06

Syringe, jumbo, borosilicate glass, with Luer-Lok tip, 100-mL, Fisher Scientific, Cat. No. 14-825-12C. As a safety precaution, the syringe may be wrapped in transparent tape.

Regulator, brass, dual-stage high-purity, for helium gas, Matheson Gas Products, Model 3122-580

Sample vials, glass vial with TFE-lined cap, 2-mL capacity, Fisher Scientific, Cat. No. 03-339

Separatory funnel, 125-mL, Pyrex, with Teflon™ plug and polyethylene stopper, Fisher Scientific, Cat. No. 10-437-5B

Support stand, with funnel support arm, Fisher Scientific, Cat. Nos. 14-668 and 14-740, respectively

Tubing, Tygon™, clear formula R-3603, ¼-inch (6.4-mm) ID, Fisher Scientific, Cat. No. 14-169-1J

Wash bottle, Nalgene™, widemouth FLPE, 500-mL, for hexane, Fisher Scientific, Cat. No. 03-409-11R

REAGENTS AND MATERIALS

The following reagents and materials are required in addition to those listed in the main method.

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.

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

L-Cysteine, 1% aqueous solution. Dissolve 10.0 ± 0.1 g of *L*-cysteine in one liter of deionized water.

Helium, high purity, 99.995%, Matheson Gas Products

Hexane, UV-grade, Burdick and Jackson, Fisher Scientific, Cat. No. 216-4

PROCEDURE

All glassware must be thoroughly cleaned by washing with 1:1 nitric acid, rinsed with water, then a rinse with acetone followed by blow-drying with nitrogen or oil-free clean air.

Sampling

Samples should be collected in a manner that assures representative sampling. **Do not collect samples in metal containers. Any mercury present will adsorb on the metal.** Samples should be collected in previously acid cleaned glass containers, approximately 500-mL in size, then shipped and analyzed as soon as possible. Samples should be kept refrigerated if stored.

Mercury Speciation

1. Filter samples by pressure filtration, if particulates are present.
 - Vacuum filtration is not to be used because the volatility of elemental mercury and light organo-mercury compounds will result in loss of the analytes.
 - Centrifugation using glass centrifuge tubes is an acceptable alternative.
2. Analyze the particulate free sample for mercury as per main body of method. This is the total soluble mercury content (T_s) (see Eq. A-3).
3. Pipet 50 mL of the filtered hydrocarbon into the 250-mL gas wash bottle.
 - The pipetted sample should contain less than 10 μg of mercury. If the sample contains more than 200 ng/mL of soluble mercury, use a smaller sample volume and dilute to 50 mL with hexane.
4. Mark the gas wash bottle with a permanent marker at the 50-mL level.
5. Connect the helium supply to the inlet side and the digital flowmeter to the exit side of the gas wash bottle. Place the bottle into an ice bath and clamp securely into position.
 - This entire gas-purge operation must be performed in a fume hood
6. Allow the sample to cool in the ice bath for approximately 30 minutes and then start the helium purge. Purge at 350 mL/min (± 20 mL/min) for 2 hours. The purged mercury will represent all the elemental mercury (A) (see Note 2 and Eq. A-3).
7. Disconnect the helium and the flowmeter from the bottle and remove it from the ice bath.
8. Add hexane through the inlet side of the gas wash bottle, using a hexane filled wash bottle, until the total volume is again equal to the original starting volume.
 - This is to correct the volume loss due to evaporation.
9. Swirl to mix while lifting and lowering the frit several times to create a homogeneous solution, then blow-dry the frit and remove it from the bottle.

10. Transfer the sample solution into a 125-mL separatory funnel containing a magnetic stirring bar and drain well.
11. Replace the top with the frit onto the gas wash bottle and pipet 25 mL of 1% *L*-cysteine solution through the inlet side of the wash bottle connected to the frit. Shake this solution well for approximately 2 minutes taking care to wet the interior glass surfaces to desorb all the mercury from the walls (see Note 2).
12. Transfer this aqueous solution into the separatory funnel and then repeat Step 11.
 - The total aqueous-phase volume will now be 50 mL.
13. Stopper the separatory funnel and place it into position on a magnetic stirrer weighted down with a lead donut as shown in Fig. A-1. Stir the two phases for 15 minutes at the highest speed necessary to create an emulsion, then place the funnel into the funnel support arm mounted on a stand and allow the phases to separate for approximately 10 minutes.
14. Drain the lower aqueous phase into a clean, dry sample bottle labeled “ionic mercury” (I).
15. If there is a significant middle emulsion layer, discard that layer to waste.
16. Drain the upper hydrocarbon sample phase into a clean, dry sample bottle labeled “non-ionic organic mercury” (O) (see Note 3).
17. Determine the mercury content of the fractions collected in Steps 14 and 15 (I and O) as per the main method.

CALCULATIONS

Calculate the amount of total combined ionic (inorganic and organic) Hg in the sample, to three significant figures, using Eq. A-1.

$$I = \frac{50C_I}{V} \quad (\text{A-1})$$

where:

C_I = measured concentration Hg from phase recovered in Step 14, ng/mL

I = total combined ionic (inorganic and organic) Hg in sample, ng/mL

V = volume of original, filtered sample extracted, mL

50 = volume in separatory funnel extracted, mL

- If the sample is undiluted, $V = 50$ and $I = C_I$.

Calculate the amount of total organic, non-ionic Hg in the sample, to three significant figures, using Eq. A-2.

$$O = \frac{50C_o}{V} \quad (\text{A-2})$$

where:

C_o = measured concentration Hg from phase recovered in Step 16, ng/mL

O = total organic, non-ionic Hg in sample, ng/mL

50 = volume in separatory funnel extracted, mL

V = volume of original, filtered sample extracted, mL

- If the sample is undiluted, $V = 50$ and $O = C_o$.

Calculate the amount of elemental Hg in the sample, to three significant figures, using Eq. A-3.

$$A = T_s - I - O \quad (\text{A-3})$$

where:

A = elemental Hg in sample, ng/mL

I and **O** = previously defined (see Eqs. A-1 and A-2)

T_s = total soluble Hg content in particulate free sample, ng/mL

NOTES

1. Symbol assignments:

T_s = total soluble mercury in particulate-free sample

A = elemental (metallic) mercury, Hg^0 (see Note 2)

O = non-ionic organic mercury species, such as dimethylmercury

I = ionic inorganic mercury (such as mercuric chloride) and ionic organic mercury species (such as methylmercury chloride)

2. The purging is done at a low temperature in order to retain volatile mercury compounds other than elemental mercury. In spite of this, the quantity of elemental mercury will also include about 30% of the dimethylmercury present. If present, about 20% of mercuric chloride will drop out of solution during the low temperature helium purge, but can be recovered from the glass walls following the 1% *L*-cysteine rinse.
3. If a low boiling compound such as dimethylmercury is present in the sample, approximately 30% of the original amount may be purged out together with the elemental mercury. Higher boiling organic mercury compounds are expected to remain in fraction O.

PRECISION

See main method.

TIME FOR ANALYSIS

The elapsed time for the analysis of a single sample is 6 hours and does not include the time required for glassware cleaning.

REFERENCE

Furuta, A., Sato, K. and Takahashi, K., *Trace Analysis of Mercury Compounds in Natural Gas Condensate*, **Proceedings of the International Trace Analysis Symposium '90**, p. 449-454, Research and Development Div., Kinuura Research Center, JGC Corporation, Sunosaki 2-110, Handa 475, Japan

SUGGESTED SUPPLIERS

In addition to the suppliers listed in the main method, the following are also suggested:

I²R-Instruments for Research and Industry, Inc., 108 Franklin Ave., Cheltenham, PA 19012 (215-379-3333)

Matheson Gas Products, P.O. Box 96, Joliet, IL 60434 (815-727-4848)

Millipore Corp., 80 Ashby Rd., Bedford, MA 01730 (617-275-9200)