



Total Mercury and Mercury Species in Liquid Hydrocarbons

UOP Method 938-20

Scope

This method is for determining total mercury in liquid hydrocarbons using a Nippon Instruments Corporation (NIC) Mercury Analyzer. The lower limit of quantitation is 0.1 ng/mL (m/v-ppb). The results can be converted to mass-ppb. *Appendix A* 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. *Appendix B* contains an alternative procedure for total mercury in liquid hydrocarbons, using different equipment from the same manufacturer with higher sensitivity. Refer to UOP Method 938-10 and earlier versions when using the NIC SP-3D Mercury Analyzer.

References

ASTM Method D4052, "Density and Relative Density of Liquids by Digital Density Meter,"
www.astm.org

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

Outline of Method

The NIC Mercury Analyzer/Model MA-3*Solo* is specified for this method. The samples are thermally decomposed in the sample heating section using the appropriate setting for each sample type. Any mercury present is atomized in the catalytic section. It is then collected and concentrated in the form of gold amalgam in the mercury collection section, which is kept at 190°C to prevent the adsorption of combustion products on the collector. After collection, the mercury is liberated by heating the collector to 600°C. The vaporized mercury is carried to an absorption cell and detected by cold vapor atomic absorption spectroscopy at a wavelength of 253.7 nm. 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, 0.1mg

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. SAFETY DATA SHEETS (SDS) OR EXPERIMENTAL SAFETY DATA SHEETS (ESDS) 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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Flask: volumetric, glass, Class A, 100-, 500-, 1000- mL, Fisher Scientific, Cat. No. 10-205C, 10-205E and 10-205F, respectively

Mercury analyzer: NIC, Model MA-3 Solo (no substitute), Nippon Instrument Corporation (NIC), with the following accessories:

Mercury Collector Tube, H-65: NIC, Cat No. W139-2300

Sample Heating Tube (Normal): NIC, Cat No. W139-1360

Sample Boat-Large Size 10pcs/set: NIC, Cat No. S-W001-0400

Joint Set: NIC, Cat No. S-W012-0100

Boat Handling Poker: NIC, Cat No. W166-0407

Nafion™ Tube 0.3m: NIC, Cat No. W121-0081-03

Air Pump: NIC, Cat No. W166-6205

Syringe, 250 µL: NIC, Cat No. S1003-6115

Micropipette, Gilson Pipetman G Series, 20-200 µL, Fisher Scientific, Cat. No. F144058MG (required for the analysis of heavy hydrocarbon and calibration samples)

Pipette tips: disposable, Fisher Scientific, Cat. No. F171300G

Pipette: volumetric, Class A, 1-mL, 5-mL and 10-mL, Fisher Scientific, Cat. Nos. 02-555-345, 02-555-351 and 02-555-356, respectively

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.

L-Cysteine: 98% purity, Pfaltz and Bauer, Cat. No. C33800

Mercuric chloride: mercury (II) chloride, Alfa Aesar Puratronic 99.999% purity, Fisher Scientific, Cat. No. 1080822

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.

Additive B: NIC, WKO-B500

Charcoal, Activated, Granular: FUJIFILM Wako Pure Chemical Corporation, Cat No.034-02125

Procedure

The analyst is expected to be familiar with general laboratory practices and the equipment being used. Portions of these procedures are specific to the specified apparatus.

All glassware including containers for samples (glass or Teflon) must be thoroughly cleaned by washing with 1:1 nitric acid, rinsing with water, rinsing with acetone, followed by blow-drying with nitrogen or oil-free clean air.

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

Alternatively, the standard solutions may be prepared from commercially available 1000-mg/L solutions provided with a certificate of analysis.

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 using Equation 1:

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

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

Mercury standard solutions with concentrations less than 0.1 mg/L - 1 month

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 or PTFE containers, 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.

Many types of samples are inhomogeneous, they should be homogenized by stirrer or ultrasonic bath before sampling. Some crude oils are solidified at room temperature and they should be homogenized in a hot-water bath at 50°C.

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.
 - Mercury Analyzer MA-3 *Solo*
 - PC (MA3SoloWin® software)
3. The message "STAND-BY xx:xx" appears at the upper left on the PC screen for 20 minutes while the optical system and the heater temperatures stabilize.
4. The system automatically starts self-diagnostics during "STAND-BY". Ensure all diagnostic self-check test parameters are passed, including leak test.
5. Confirm the conditions required for the analysis as indicated in Table 1.

Table 1
Initial Conditions

Decomposition catalyst	H2	580°C
Mercury collector	H3	190°C

Optical unit
Air

H4

150°C
Purified air (0.2L/min)

- Set the heating speed of the mercury collection section for measurement in accordance with the mercury content. The guidelines are as follows:

LOW: 0 to 100 ng using linear equation

0 to 1,000 ng using cubic equation

HIGH: 0 to 1,000 ng using linear equation

0 to 10,000 ng using cubic equation

- Create the heating method as indicated in Table 2.

Table 2				
Heating Method				
Sample Type	Step	Temperature (°C)	Heating Time (sec)	Duty (%)
STD	Atomize 1	0	0	0
	Atomize 2	0	0	0
	Atomize 3	800	240	100
HEAVY OIL	Atomize 1	0	0	0
	Atomize 2	350	180	70
	Atomize 3	850	360	100
LIGHT OIL	Atomize 1	80	60	0
	Atomize 2	350	120	70
	Atomize 3	800	300	100

Calibration

It is recommended the analyzer be calibrated before analyses. To create the calibration curve, the measurement of at least three mercury standards is recommended. Use Table 3 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 µL of sample (~10 ppb mercury), use the 1.5 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-µL additions of the standard as shown in Table 3 and according to the following procedure.

Reduction of System Blank

- Prepare three sample boats.
 - Put the boat on boat in/out rod to start measuring under “1: STD” method.
 - Confirm the boat blank is low enough for your intended samples.
- For lowest samples, PEAK ABS should be lower than 0.00002, preferably.

Calibration curve

- Select “1: STD” on the “Method Set” and select the last one of above measurements for blank and three or more standards according to Table 3.
- Enter the necessary numbers in the ANALYSIS table and then tick them.
- Three calibration curves are provided, but “y=ax+Blank” is usually recommended. When

standard samples are measured, the calibration curve is automatically updated. The measurement results are registered in the Table window.

Table 3
Calibration Ranges and Standards

<u>Measuring Range, ng</u>	<u>Standard Solution, mg/L</u>	<u>Standard Solution Injection Volume, μL</u>
0 – 1.5 (Low)	0.01	50, 100, 150
0 – 15 (LOW)	0.1	50, 100, 150
0 – 90 (LOW)	1.0	30, 60, 90
0 – 900 (HIGH)	10	30, 60, 90

Analysis of Light Hydrocarbons

Samples that contain volatile material, e.g., naphtha, gasoline, jet fuel, are analyzed using this procedure.

1. Prepare three boats filled $\sim 80\%$ with Additive B, as shown in Figure 1, and measure the blanks one by one using LIGHT OIL Heat Method. The reason to use 3 sets of sample boats is to allow enough cooling time between each analysis, preventing against loss of mercury due to injecting sample into a hot sample boat.

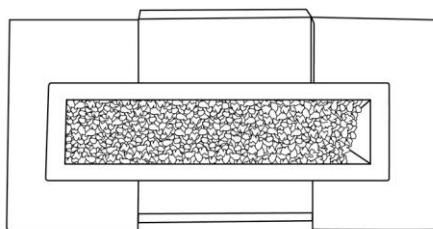


Figure 1 Boat $\sim 80\%$ Filled with Additive B

2. Select the last two blanks of Additive B as “R.Blank” in SAMPLE TABLE.
3. Samples should be well mixed by hand-shaking or light ultrasonic agitation, approximately 1 minute, before sampling.
4. Take the sample with a gas-tight syringe. Permitted sample volume is up to 200- μ L per analysis, depending on its Hg concentration.
5. Take the first sample boat, insert the syringe needle to the bottom of the boat, as shown in Figure 2, before injecting the sample into it.

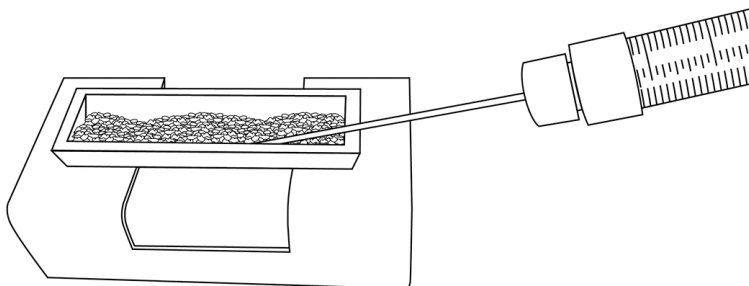


Figure 2 Syringe placement for Sample Injection

6. Using the tongs provided, transfer the sample boat with sample onto the inlet poker and insert into the MA-3 Solo furnace for analysis.
 - **Caution: DO NOT MAKE** the sample injection with the sample boat placed on the Inlet Poker. The heat from the poker arm and the furnace surrounding may cause “Flashing” to the liquid hydrocarbons due to its volatility.
7. Select “LIGHT OIL” on the SAMPLE Table and START.
8. If the density is known, enter it in the Nippon instrument software SAMPLE TABLE for reporting the Mercury concentration in mass-ppb. An example entry is shown in Figure 3.

No.	MEAS	METHOD	NAME	SVOL [uL]	DENSITY [Kg/L]	LOW AREA-ON	MEAS [ng]	CONC [ug/kg]	RECOVERY [%]	OX
1	☐	5:Light Oil	NAP 4	250.000	0.700	0.064418	0.608	3.474	-	o
2	☐	5:Light Oil	NAP 4	250.000	0.700	0.062895	0.593	3.389	-	o
3	☐	5:Light Oil	NAP 4	250.000	0.700	0.062033	0.585	3.343	-	o

Figure 3 Example entry into Nippon Instrument Software SAMPLE TABLE

9. After the analysis, the sample boat with Additive B can be reused for additional analysis after cooling, daily or as long as the Mercury blank remains low and is not affecting the sample results.
 - It is a good practice to analyze a standard as a sample 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.
 - Duplicate analyses may be performed in order to increase confidence in the results.
10. Repeat steps 3 – 8 for each remaining sample using a room temperature boat every time.

Analysis of Condensate

1. Prepare three boats filled ~80% with Additive B and measure the blanks one by one.
2. Select the last two blanks of Additive B as “R.Blank” in SAMPLE TABLE.
3. Samples should be well mixed by hand-shaking or light ultrasonic agitation (~2 minutes) before sampling.
4. Take the sample with a gas-tight syringe. Permitted sample volume is up to 200-μL per analysis, depending on its Hg concentration.
5. Take the 1st sample boat, insert the syringe needle to the bottom of the boat before injecting the sample into it (see Figure 2).
6. Using the tongs provided, transfer the sample boat with sample onto the inlet poker and insert into the MA-3 Solo furnace for analysis.
 - **Caution: DO NOT MAKE** the sample injection with the sample boat placed on the Inlet Poker. The heat from the poker arm and the furnace surrounding may cause “Flashing” to the liquid hydrocarbons due to its volatility.
7. Select “2: SOLID/HEAVY OIL” on the SAMPLE TABLE and START.
8. Enter the density to convert mass-ppb as above for reporting the Mercury concentration in mass-ppb.
 - It is a good practice to analyze a standard as a sample 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.

- Duplicate analyses may be performed in order to increase confidence in the results.
9. Repeat steps 3 – 8 for each remaining sample using a room temperature boat every time.

Analysis of Heavy Hydrocarbons

Since most Crude and Fuel oils have high viscosity (waxy) and they are sometimes solidified at room temperature making them especially non-homogeneous, they should be melted/dissolved and homogenized before sampling.

1. The container is put on the hot-plate/water-bath set at 50°C for a few minutes until fully melted as liquid. Stir/shake it well. For non-waxy light Crude oils, they can skip this melting step.
2. Prepare three boats filled with activated charcoal as shown in Figure 4 and measure the blanks one by one. Select the last two blanks of Charcoal as “R.BLANK” in SAMPLE TABLE. The Charcoal Pellets are for single analysis of a Blank or Sample, and are not reusable.

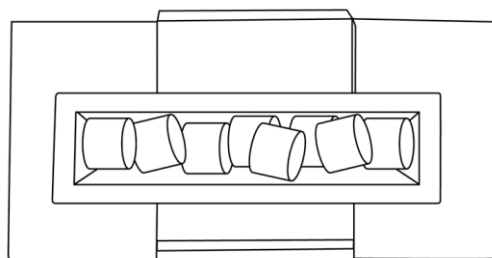


Figure 4 Sample Boat with Activated Charcoal pellets

3. For Heavy-Hydrocarbon sample, it is recommended to take the amount gravimetrically. Due to its non-homogeneity, the sample should be collected with a Pasteur Pipette (Dropper) or with a micro-pipette, and not by syringe.
4. Tare the boat filled with the Charcoal pellets in an analytical balance. Carefully drip and spread the sample over the Charcoal pellets as shown in Figures 4 and 5. Avoid dropping sample on the boat edge if possible. Record the sample amount indicated on the balance. Recommend maximum amount per analysis is up to 200 mg, depending on the Mercury concentration.

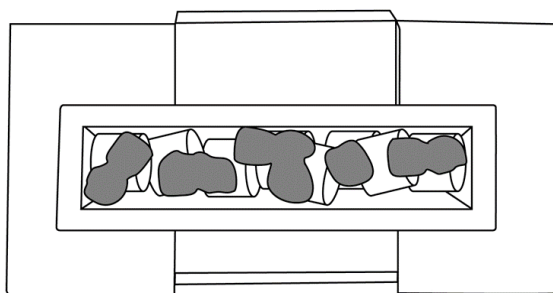


Figure 5 Sample Boat with Charcoal Pellets and Sample

5. Using the tongs provided, transfer the sample boat with sample onto the inlet poker and insert into the MA-3 Solo furnace for analysis.
6. Select “SOLID/HEAVY OIL” on the SAMPLE TABLE and start.
 - It is a good practice to analyze a standard as a sample 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.

- Duplicate analyses may be performed in order to increase confidence in the results.

7. Repeat steps 3 – 6 for each remaining sample using a room temperature boat and fresh Charcoal pellets every time.

Calculations

All calculations are performed by the MA3SoloWin[®] software. Light hydrocarbons are usually 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 µg/g (mass-ppm).

Precision

Repeatability

To evaluate the practical LOD (Limit of Detection) and LOQ (Limit of Quantification), an actual Naphtha is analyzed repeatedly. LOD is defined to be 3×SD (Standard deviation) and LOQ is 10×SD. Table 4 lists the Limits of Detection and Quantification

Table 4 Limit of Detection and Quantification					
<u>Amount (µL)</u>	<u>n</u>	<u>Average µg/kg</u>	<u>SD (µg/kg)</u>	<u>LOD (µg/kg)</u>	<u>LOQ (µg/kg)</u>
250	9	0.163	0.02	0.073	0.24

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.

Time for Analysis

The elapsed time for calibration is 36 minutes and for one analysis is 10 minutes. The labor requirement is 10 min.

Suggested Suppliers

Fisher Scientific, 585 Alpha Dr., Pittsburgh, PA 15238 (412-490-8300) www.fishersci.com

FUJIFILM Wako Pure Chemical Corp.: 1-2, Doshomachi 3-chome, Chuo-ku, Osaka, 540-8805, Japan, (06-6203-3741)

Matheson Tri-Gas, 166 Keystone Drive, Montgomeryville, PA 18936 (215-648-4000)
www.mathesontrigas.com

Nippon Instruments Corp.: 14-8 Akaoji, Takatsuki, Osaka, 569-1146, Japan (0726 93-6863)

Pfaltz and Bauer: 172 E. Aurora St., Waterbury, CT 06708 (203-574-0075)

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

Appendix A

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.

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

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. The purged sample is then extracted with a 100 ppm sodium chloride 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 body of the 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 round, Qorpak, Poly-Seal™ lined closures, 60- and 480-mL, Fisher Scientific, Cat. Nos. 02-992-839 and 02-992-208, respectively

Dish, crystallizing, Kimax™, 170 x 90 mm, Fisher Scientific, Cat. No. 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. 10-205F

Flow Controller, FM 1050 Flowmeter with #602 (E300) 150-mm tube and glass float ball. 350 mL/min of helium is 129 mm on this tube. Matheson

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, Glas-Col, Fisher Scientific, Cat. No. 108B-LD-5C

Magnetic stirrer, Fisher Scientific, Cat. No. 90-691-16

Magnetic stir bars, PTFE starburst stirring heads, 19-mm diameter, Fisher Scientific, Cat. No. 14-513-76 (must fit inside separatory funnel)

Marker, permanent, local supply

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, 0.2-micron, 25-mm diameter, PTFE, Fisher Scientific, Cat. No. 09-730-19

Syringe, polypropylene barrel, polyethylene plunger, with Luer-Lok tip, 30- and 50-mL, Fisher Scientific, Cat. Nos. 14-817-41 and -40, respectively

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

Sample vials, glass, with TFE-lined cap, 2-mL capacity, Fisher Scientific, Cat. No. 03-339-21A

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. 14-679Q and 14-740Q, respectively

Timer, capable of timing two hours, Fisher Scientific, Cat. No. 06-662-45

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

Wash bottle, Nalgene™, widemouthed FLPE, 500-mL, for isooctane, Fisher Scientific, Cat. No. 03-409-12E

Reagents and Materials

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

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

Helium, high purity, 99.995%

Isooctane (2,2,4-Trimethylpentane), >99.0%, B&J Brand, VWR, Cat. No. BJ-362-4

Sodium Chloride, Fisher Scientific, Cat No. S271-1

Sodium Chloride, 100 ppm aqueous solution. Dissolve 0.100 ± 0.01 g of sodium chloride in one liter of deionized water.

Water, deionized or distilled

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 or PTFE containers, 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 Equation A3).
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 isooctane.
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
 - All purging apparatus must be considered to be contaminated with mercury. All purging apparatus must be reserved for this analysis.
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 ($\pm$ 20 mL/min) for 2 hours. The purged mercury will represent all the elemental mercury (**A**) (see Note A2 and Equation A3).
7. Disconnect the helium and the flowmeter from the bottle and remove it from the ice bath.
8. Add isooctane through the inlet side of the gas wash bottle, using an isooctane 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 100 ppm sodium chloride 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 A2).
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 Figure A-1. Stir the two phases for 15 minutes at the 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 A3).
17. Determine the mercury content of the fractions collected in Steps 14 - 16 (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 Equation A1.

$$I = \frac{50 C_i}{V} \quad (\text{A1})$$

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 Equation A2.

$$O = \frac{50 C_o}{V} \quad (\text{A2})$$

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 Equation A3.

$$A = T_s - I - O \quad (\text{A3})$$

where:

A = elemental Hg in sample, ng/mL

I and **O** = previously defined (see Equations A1 and A2)

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

Notes

A1. Symbol assignments:

T_s = total soluble mercury in particulate-free sample

A = elemental (metallic) mercury, Hg⁰ (see Note A2)

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)

A2. 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 100 ppm sodium chloride rinse.

- A3. 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.

Suggested Suppliers

The following suppliers are suggested in addition to those listed in the body of the method.

Glas-Col, LLC, 711 Hulman Street, Terre Haute, IN 47802-0128 (812-235-6167) www.glascol.com

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

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

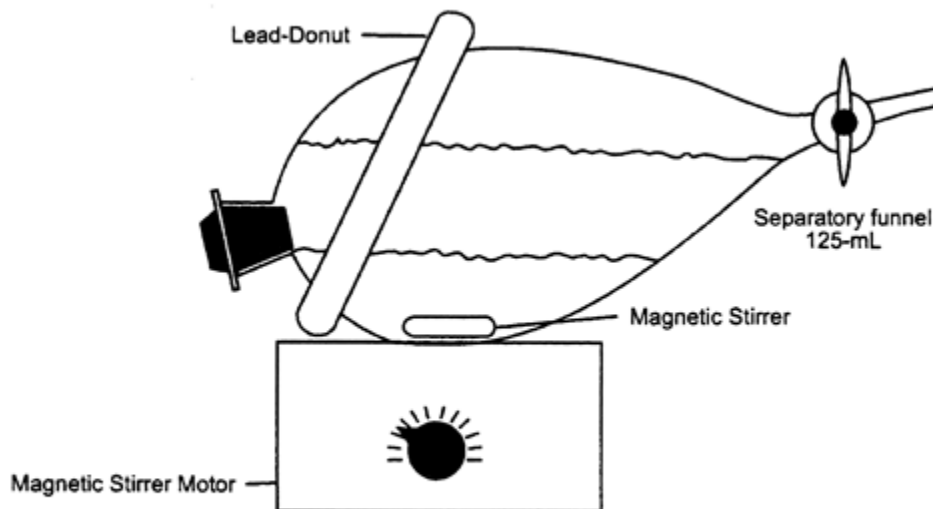


Figure A-1

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

Appendix B

Total Mercury in Liquid Hydrocarbons using the NIC PE-1000 Mercury Analyzer

Scope

This method is for determining total mercury in liquid hydrocarbons using a Nippon Instruments Corporation (NIC) Mercury Analyzer/Model PE-1000, equipped with an automatic sample changer. The method may be applied to samples containing 0.01 to 10,000 ng/mL (m/v-ppb). The results can be converted to ng/g (mass-ppb).

Outline of Method

The NIC Mercury Analyzer/Model PE-1000, consisting of an automatic sample changer and mercury measuring equipment, is specified for this method. Samples are dispensed with a syringe inside the auto sample changer, and then injected into the sample heating section of the mercury analyzer. The samples are thermally decomposed in the sample heating section. Any mercury present is atomized in the catalytic section and then collected and concentrated in the form of gold amalgam in the mercury collection section. The mercury is released and atomized again by heating, and then detected using atomic fluorescence spectroscopy at a wavelength of 253.7 nm in the fluorescence cell of the detector. After preparing the samples in the vials, all operations from the sample decomposition process to the mercury detection and calculation are carried out automatically by the instrument.

Apparatus

The following apparatus are an addition or substitution to that listed in the body of the method.

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

Mercury analyzer, NIC, Model PE-1000 (no substitute), with the following accessories:

Air purifier, NIC, Cat. No. S1063-0510-00

Collector tube, quartz, NIC, Cat. No. Model M100, S1085-0820-00

Sampling heating tube, NIC, Cat. No. S1085-0810-00

Reagent poker, NIC, Cat. No. N-8915-1801

Silicone septum, NIC, Cat. No. GLS-3007-18115

Quartz wool, 1g/1pk, NIC, Cat. No. S1003-6114-00

O-ring, P-8 Viton™, NIC, Cat. No. VLQ-P-8-F

PFA tube, 2X4, NIC, Cat. No. TUK-PFA 2X4

PP tube, 2X4, NIC, Cat. No. KNI02-2X4

PTFE tube, 2X4, NIC, Cat. No. TUK-PTFE 2X4-K

Nylon tube, 4X6, NIC, Cat. No. NMA-N2-4-6X4-1

Nylon tube, 5X7, NIC, Cat. No. KK1-001-577-1

Joint, PL 1/4-01, NIC, Cat. No. PAS-PL1/4-01

Joint, 30-4U-S, NIC, Cat. No. FLW-30-4U-S

Joint, SFH-12-R1/4, NIC, Cat. No. FLC-1062-10

Joint, 30-4UE-C, NIC, Cat. No. FLW-30-4UE-C

Jacket heater, NIC, Cat. No. N-1085-9615-300

Sample inlet, NIC, Cat. No. S1085-0810-00

Vial with cap and septum, NIC, Cat. No. 81085-6105-11

Syringe, NIC, Cat. No. HML-1710N

Scrubber bottle with cap and packing, NIC, Cat. No. S1085-6103-11

Waste bottle with cap and packing, NIC, Cat. No. S1085-6104-11

Regulators, stainless steel, dual-stage high purity, for argon and compressed air, Matheson Tri-Gas, Models 3810-580 and -590, respectively

Reagents and Materials

The following reagents and materials are an addition or substitution to that listed in the body of the method.

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

Argon, purity 99.99%

Air, dried

Isopropyl alcohol (2-propanol), 99.5%, Fisher Scientific, Cat. No. AC412975000

Toluene, 99.5%, Fisher Scientific, Cat. No. AC421175000

Procedure

All glassware must be thoroughly cleaned by washing with 20:1 nitric acid, rinsed with water, followed by blow-drying with nitrogen or oil-free clean air.

Preparation of L-Cysteine Solution and Standards

Prepare the L-cysteine and standard solutions as described in the body of the method. The standard solutions may also be prepared from commercially available 1000-mg/L solutions provided with a certificate of analysis. Storage and shelf life recommendations are the same as in the body of the method.

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 or PTFE containers, and 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.
Automatic Sample Changer HT-300A
Mercury Analyzer PE-1000
PC (PE1000Win^R software)
3. The message "STAND-BY xx:xx" on the PC screen appears at the upper left for 20 minutes while the optical system and the heater temperatures stabilize.
4. Confirm the conditions required for the analysis as indicated in Table B1.

Table B1
Initial Conditions

Mercury compounds trap H1	220°C
Decomposition catalyst H2	600°C
Decomposition catalyst H3	400°C
Jacket heater H4	200°C
Mercury collector temperature H5	200°C

- If the instrument is not used for some time, there is a sleep function that will turn the heaters and lamp off to conserve them. Or the instrument may be turned off. In any case, air and argon pressure must be maintained.
5. Check the instrument for leaks in the argon and air path according to the instructions on the PC screen.
 6. Set the heating speed of the mercury collection section for measurement in accordance with the mercury content. A guideline for that is as follows:

Low mercury (0 to 10 ng): The heater H5 of the mercury collection section heats up at full power and the mercury is quickly released into the fluorescence cell.

High mercury (10 to 100 ng): The heater H5 of the mercury collection section slowly heats up and the mercury is gradually released into the fluorescence cell.

Calibration

It is recommended that the analyzer be calibrated before analyses. To create the calibration curve, the measurement of at least three mercury standards is recommended. Use Table B2 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 B2 and according to the following procedure.

System Blank

1. Set a sample vial filled with IPA (isopropyl alcohol) onto the sample tray of the automatic sample changer.
2. Enter the vial numbers in the sample table of the PE1000Win^R software and then select them.

3. Select “0: NAPHTHA” on the “Method Set” mode and run IPA several times to reduce the blank to less than 20 counts as integral value.
 - This is to expel any mercury gas remaining in the analyzer.

Calibration curve

1. Prepare mercury standard solutions at 5.0, 0.1, and 0.01 mg/L as described in the body of the method. Prepare a 0.5 mg/L mercury standard solution by pipetting 10 mL of the 5-mg/L mercury standard solution prepared in the body of the method into a 100-mL volumetric flask. Dilute to volume with the 10-mg/L L-cysteine solution prepared in the body of the method.
 - The actual concentration of the 0.5-mg/L standard will be one-tenth of the standard being diluted.
2. Place an aliquot of the standard solutions and deionized water in the sampler vials and place them on the sample tray of the automatic sample changer.
 - Do not fill the vials more than approximately 80% full.
3. Select “1: WATER” on the “Method Set” mode and run deionized water for blank and three or more standards according to Table B2.
4. Enter the vial numbers in the sample table of the PE1000WinR software and then select them.
5. Three calibration curves are provided, but “ $y=ax+Blank$ ” is usually recommended. When standard samples are measured, the calibration curve is automatically updated. The measurement results are registered in the sample table window.

Table B2
Calibration Ranges and Standards

<u>Measuring Range, ng</u>	<u>Standard Solution, mg/L</u>	<u>Standard Solution Injection Volume, μL</u>
2 (Low)	0.01	50, 100, 150
20 (High)	0.1	50, 100, 150
100 (High)	0.5	50, 100, 150

Analysis of Light Hydrocarbons

Samples that contain volatile material, e.g., clean naphtha or gasoline, are analyzed using this procedure.

1. Place an aliquot of the samples in the sampler vials and place them on the sample tray of the automatic sample changer.
 - Do not fill the vials more than approximately 80% full.
2. Enter the vial numbers in the sample table of the PE1000WinR software and then select them.
3. Select “0: NAPHTHA” on the “Method Set” mode and run.

Analysis of Condensate

1. Place an aliquot of the samples in the sampler vials and place them on the sample tray of the automatic sample changer.
 - Do not fill the vials more than approximately 80% full.
2. Enter the vial numbers in the sample table of the PE1000Win^R software and then select them.
3. Select “2: CONDENSATE” on the “Method Set” mode and run.

Analysis of Heavy Hydrocarbons

Since high-viscosity samples such as crude oil can't be pulled in by the syringe, the sample should be diluted (~1/5) with toluene using this procedure.

- Confirm that the toluene is mercury-free by analyzing it as described under *Analysis of Light Hydrocarbons*.
- Determine the density of the sample using ASTM Method D4052, "Density and Relative Density of Liquids by Digital Density Meter," or other reliable procedure.
 - Tare an empty autosampler vial to the nearest 0.1 mg. Add 0.6 ± 0.1 g of sample and reweigh. Add toluene until the vial is about 80% full and reweigh.
 - Determine the density of the mixture using Equation B1.

$$\text{Density of sample mixture} = \frac{F + G}{\frac{F}{D} + \frac{G}{E}} \quad (\text{B1})$$

where:

- D** = density of sample, g/mL
E = density of toluene, 0.866 g/mL
F = mass of sample weighed into vial, g
G = mass of toluene weighed into vial, g

- Enter the mass of the sample in the vial, the mass of the sample plus toluene added to the vial, and the calculated density of the mixture into the software SMP table. An example entry is shown in Figure B1.

No.	Meas	Vial Number	Method Number	Multiple Injection	Meas Range	NAME	Sample [g]	Total [g]	SVOL [uL]	DENSITY	INTEGRAL [Low][OFF]	HG [pg]	CONC [ug/kg]
1	☒	00	3: CRUDE OIL	1		Crude Oil ABC	0.582	1.255	100.000	0.872			

Figure B1

Example Entry into Software SMP Table

- Set the filled vials in the sample tray and enter the vial numbers in the sample table of the PE1000Win^R software and then select them.
 - It is a good practice to analyze a standard as a sample 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 standard or a 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 PE1000Win^R software. Non-diluted samples are usually reported as ng/mL (m/v-ppb) or µg/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 µg/g (mass-ppm). Report results to three significant figures.

Precision

Analysis of the samples used for this precision statement were performed by the vendor. The precision statements were determined using UOP Method 999.

Repeatability, Site precision, and Reproducibility

A nested design was carried out for determining trace mercury for two samples with two analysts in each of eight laboratories. Each analyst carried out tests on two separate days, performing two tests each day. The total number of tests performed was 128. Using a stepwise analysis of variance procedure, the within-day estimated standard deviation (esd) was calculated and is listed in Table B3. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference shown in Table B3 with 95% confidence. Two tests performed in the same laboratory by different analysts on different days should not differ by more than the site precision allowable difference shown in Table B3 with 95% confidence. Two tests performed in different laboratories by different analysts on different days should not differ by more than the allowable difference shown in Table B3 with 95% confidence.

The data in Table B3 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.

Table B3

Repeatability, Intermediate Precision, and Reproducibility, Hg, ng/mL

<u>Mean Concentration</u>	<u>Repeatability</u>		<u>Site Precision</u>		<u>Reproducibility</u>	
	<u>Within- Day esd</u>	<u>Allowable Difference</u>	<u>Within- Lab esd</u>	<u>Allowable Difference</u>	<u>Between- Lab esd</u>	<u>Allowable Difference</u>
0.28	0.011	0.03	0.017	0.05	0.034	0.10
12.14	0.147	0.42	0.181	0.53	0.379	1.14

Time for Analysis

The elapsed time for one analysis including calibration is 0.5 hour. The labor requirement is 0.2 hour.