



A Honeywell Company

Total Mercury in Solids

UOP Method 1009-15

Scope

This method is for determining total mercury in solid materials using a Nippon Instruments Corporation (NIC) MA-3000 Mercury Analyzer. The instrument uses a dual path detector to measure from the lower limit of 0.1 ng/g (mass-ppb) to an upper limit of 500 µg/g (mass-ppm), when analyzing a 50 mg sample. This procedure can also be used for aqueous liquid samples and high boiling hydrocarbons (such as crude or shale oil) through the use of appropriate combustion programs. Volatile hydrocarbons (e.g. naphtha and BTX aromatics) should be analyzed by UOP Method 938.

References

UOP Method 938, "Total Mercury and Mercury Species in Liquid Hydrocarbons," www.astm.org

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

Outline of Method

The NIC Mercury Analyzer/Model MA-3000, consisting of an autosampler, a mercury atomizer and integrated mercury detector, is specified for this method. The sample is decomposed by heating in oxygen and the mercury vapor in the gaseous products is trapped by the mercury collector as gold amalgam. The temperature of the mercury collector is kept at 210°C to prevent the adsorption of non-mercury combustion products on the collector. After collection, the mercury is liberated by heating the collector to 700+°C. The vaporized mercury is carried to a dual absorption cell (long and short path lengths) with a pure oxygen carrier gas and detected by the cold vapor atomic absorption technique. After introducing the sample into boats and loading the autosampler rack, all operations from the sample decomposition process to the mercury detection and calculation are carried out automatically by the instrument. The instrument collects data from both cells, and the selection of High or Low range can be changed by the operator after the sample analysis has completed.

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 0.01-mg, Mettler-Toledo XA105 or equivalent. If a different balance is used, it should be one that will directly communicate with the MA3Win software.

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 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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Cylinder, graduated, 500-ml, Class B, VWR, Cat. No. 89000-258

Desiccator, VWR, Cat. No. 25031-048 (Corning 3120-250), optional

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

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

Gloves, thermal protection, VWR, Cat. No. 32885-407, optional

Mercury analyzer, NIC, Model MA-3000 (no substitute), with the following accessories:

Boats, ceramic, for MA-3000, NIC, Cat. No. S1106-6100-00

Sample heating tube MA-3, NIC, Cat. No. S1106-0620-00. Tubes with catalyst for Appendix K should be used with high halogen samples.

Sample boat fixture (for measurement), NIC, Cat. No. N-1106-901-400

Mortar and Pestle, Agate, Fisher Scientific, Cat. No. 12-950B

Pipet, digital, variable volume 20-200 µL, Fisher Scientific, Cat. No. 21-377-289 (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

Pipet filler, Fisher Scientific, Cat. No. 13-681-51

Refrigerator, explosion proof or flammable storage

Regulator, 2-stage Stainless Steel, CGA 540, Matheson Cat. No. 3810-540

Sample containers, glass or Teflon™ bottles, acid cleaned, see *Procedure*

Tongs, crucible, VWR, Cat. No. 82027-372, for muffle furnace use

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, 500-mL, for acetone, Fisher Scientific, Cat. No. 03-409-11A

Wash bottle, Nalgene, Right to Know Safety, 500-mL, for water, Fisher Scientific, Cat. No. 03-409-11E

Reagents and Materials

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

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

Aluminum Foil, local supply, optional

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

Mercuric chloride, mercury (II) chloride, 99.999% purity, Sigma-Aldrich, Cat. No. 20-377-7 (Note: Toxic material, review SDS before handling and wear appropriate personal protective equipment)

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

Nitric Acid, 1:1. Combine 200 mL of concentrated nitric acid with 200 mL of water in a plastic wash bottle, swirl to mix, and use freshly prepared while still warm.

Nitrogen, or oil-free clean air, for blow drying glassware

Oxygen, UHP, Airgas Cat. No. OX UHP200

Pipet tips, disposable, Fisher Scientific, Cat. No. 21-377-45

QC standard, a certified Hg standard should be obtained for use as a Quality Control (QC) standard. An example is NIST 1632d (Trace Elements in Coal) at 0.0928 mg/kg Hg.

Transfer pipets, disposable, Fisher Scientific Cat. No. 13-711-9AM

Water, deionized or distilled. Certified low Hg reagent water can be purchased from O2SI, Cat. No. 190007-16

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

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.

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. Mercury present can adsorb on the metal.** Liquid samples must be collected in previously acid cleaned glass containers and then analyzed as soon as possible.

Instrument Set Up

1. Set up the instrument according to the manufacturer's instructions.
2. Turn on the power to the instrument and start the MA3Win control software on the PC.
 - The instrument is normally turned off overnight and when not in use.
 - Standard operating conditions are shown in Table 1.
3. Allow the instrument to stabilize. The instrument software will display a timer to show remaining stabilization time.

Table 1
Operating Conditions

Idle Temperature of sample heating furnace	150°C
Temperature of decomposition furnace element (front zone)	560°C
Temperature of decomposition furnace element (back zone)	300°C
Pre-heating temperature of mercury collector	210°C
Mercury collector desorb temperature	700+°C
Detector Temperature	150°C
Carrier gas	Oxygen, min. purity 99%
Carrier gas pressure	50 kPa
Combustion (Decomposition) flow rate	0.4 L/min
Measuring system flow rate (AAS)	0.5 L/min
Analysis time (dependent on heating method)	~10 min

4. Perform a system leak check from the MA3Win software menu (Run → Leak Check). Once flow stabilizes at 0.4 ± 0.01 L/min, click “START”.
 - The flow should decrease to a level at or below 0.02 L/min within 1 minute. If this does not occur, then the instrument should be turned off and allowed to cool before checking the instrument for loose joints or damaged tubes.
 - The instrument must pass the leak test before it can be calibrated or used to analyze samples.
5. In addition to the factory pre-defined decomposition methods, a new method needs to be created for catalysts, adsorbents and heavy hydrocarbons as shown in Table 2.

Table 2
Catalyst Method Conditions

Atomize 1 Heat Temperature	150°C
Atomize 1 Heat Time	60 s
Atomize 1 Start Duty	5%
Atomize 1 Max Duty	5%
Atomize 1 Slope Time	60 s
Atomize 2 Heat Temperature	350°C
Atomize 2 Heat Time	120 s
Atomize 2 Start Duty	30%
Atomize 2 Max Duty	30%
Atomize 2 Slope Time	0 s
Atomize 3 Heat Temperature	850°C
Atomize 3 Heat Time	300 s
Atomize 3 Start Duty	10%
Atomize 3 Max Duty	100%
Atomize 3 Slope Time	90 s
Atomize Step 4 is not used	

Preparation of L-Cysteine Solution and Standards

L-Cysteine Solution, Approximately 100-mg/L

1. Weigh approximately 0.10 g of L-cysteine, to the nearest 0.1 mg, onto a weighing paper.
2. Transfer quantitatively with deionized water into a 1000-mL volumetric flask. Pipet 2 mL of concentrated nitric acid and dilute to the mark with deionized 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 100-mg/L L-cysteine solution into a 500-mL (0.5-L) volumetric flask.
3. Dilute to the mark with the 100-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 100-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 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 100-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 100-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 100-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 0.001-mg/L

3. Pipet 10 mL of the 0.01-mg/L mercury standard into a 100-mL volumetric flask.
4. Dilute to volume with the 100-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:

100-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

Analysis of Solid Samples

Inorganic solid samples, such as catalysts and adsorbents should be ground to a fine, homogeneous powder using a mortar and pestle. Agate mortar and pestle sets are recommended to minimize the loss of Hg and to prevent sample cross-contamination. Metal grinding vessels and mechanical grinders should not be used, due to the potential for loss of Hg during grinding.

Analysis of Liquid Hydrocarbons

Samples that contain volatile material, e.g., gasoline, are analyzed using UOP Method 938. Less volatile hydrocarbons, e.g., kerosene, diesel, and heavier, can be analyzed using this procedure. When analyzing liquids, it is recommended that only 1 tray of sample boats should be loaded at a time.

Preparation of Sample Boats

Boats can be pretreated to remove Hg by cycling through the instrument using an analysis method with a decomposition step of at least 800°C. The use of a separate muffle furnace is also acceptable.

1. Set the muffle furnace temperature at $750 \pm 50^\circ\text{C}$.
2. Place sample boats to be used for the analysis in the muffle furnace.
3. Heat boats for at least 2 hours in the muffle furnace.
4. Cool in a dessicator before placing the boats on the sample trays in the instrument.

Calibration

It is recommended that the analyzer be calibrated regularly, either based on the Control Chart of a QC reference or on a timed schedule during times when samples are being analyzed. The vaporized Hg passes through both cells, so the instrument calibration can include standards for both the Low and High range calibrations. To create each calibration curve, the measurement of three mercury standards is recommended. Use Table 3 to select the appropriate range, standard solutions and injection volumes. For high level calibrations where standards above 10.0 mg/L are used, then calibrate for High range Hg only, up to a maximum of 25.0 µg per measurement. The calibration slope must be between 0.7 and 1.3, otherwise the instrument will return a warning message.

Table 3
Calibration Ranges and Standards

<u>Measuring Range</u>	<u>Standard Solution, mg/L</u>	<u>Standard Solution Injection Volume, µL</u>
Low	0.001	50, 100
	0.01	50, 100, 200
	0.10	50, 90

High	0.10	100, 200
	1.00	50, 100, 200
	10.0	50, 100, 200
	Higher standards can be added up to a maximum of 25.0 µg of Hg (250 µL of 100 mg/L)	

- Remove the sample tray from the rack inside the autosampler. If the boats were pretreated in the muffle furnace, place boats on the tray in each of the 10 positions.
 - Tweezers must be used when handling the boats.
 - Close the cover to the autosampler when not actively adding or removing trays.
 - Place the sample tray on a clean surface, such as aluminum foil or paper, to prevent contamination.
- Add, using a digital pipet, the appropriate volume of the mercury standards to each boat on the tray.
 - The first three boats on the first sample tray are left empty to serve as the calibration blank.
 - Table 3 serves as a guide to determine the volumes to be added.
 - It is recommended to analyze at least two sample boats with each injection volume.
 - Liquid volumes should not exceed 250 µL.
- Enter the standard information into the MA3Win table (left tab for “STD”). Use the pre-defined analysis method “STD” for the aqueous calibration standards.
- Click in the STD [ng] column to open the “STD INPUT” window and enter the standard concentration and injection volume. Repeat for each standard on the sample tray.
- Repeat Steps 1 through 4 for the remaining calibration samples.
- Click the “MEASURE” box in the left column next to each standard to be analyzed then click the “START” icon to begin the calibration. The calibration will proceed automatically until the final standard has been measured.
 - 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.
- Recondition all of the boats used for the calibration prior to re-using the boats for sample analysis.

Sample Analysis (Inorganic Solids)

- Place the Sample boat fixture (for measurement) on the weighing platform of the balance.
- Remove the sample tray from the rack inside the autosampler. If the boats were pretreated in the muffle furnace, place boats on the tray in each of the 10 positions.
 - Tweezers must be used when handling the boats.
 - Close the cover to the autosampler when not actively adding or removing trays.

- Place the sample tray on a clean surface, such as aluminum foil or paper, to prevent contamination.
3. Place the second sample boat on the balance and tare
 - The first boat is used as a conditioning blank.
 4. Set up the sample table (right tab in MA3Win). The first position is the conditioning blank; positions 2, 3 and 4 are set for the QC sample. Samples are added to the table in triplicate.
 5. In the “METHOD NUMBER” column, select the catalyst method as described in Table 2 above.
 6. In the sample size (SVOL [mg]) column of the first QC sample, right click and select the option “Balance Volume Set” to enable direct transfer of the sample mass from the balance into WA3Win.
 - Alternatively, sample mass can be typed directly into the table, but the direct communication from the balance minimizes transcription errors.
 7. Carefully transfer approximately 50 mg of sample into the boat and press the print button to transfer the sample size from the balance into MA3Win.
 - For samples above 200 µg Hg/g, the sample size should be reduced to 15 - 20 mg. Smaller sample sizes can be used to extend the calibration above 500 µg/g, up to a maximum of 25 µg of Hg per measurement.
 8. Repeat until all sample boats in the tray have been loaded. Continue with additional trays as needed.
 - It is a good practice to analyze a QC standard in the beginning of the run before the first sample to ensure that the equipment is functioning properly. After the first sample tray, load 3 samples in triplicate with the last position reserved for the QC standard.
 - Triplicate analysis is recommended to prevent any sample inhomogeneity from affecting the results.
 9. Click the “MEASURE” box in the left column next to each sample to be analyzed then click the “START” icon to begin the analysis. The analysis will proceed automatically until the final sample has been measured.

Sample Analysis (Heavy Hydrocarbons)

1. Place the Sample boat fixture (for measurement) on the weighing platform of the balance.
2. Remove the sample tray from the rack inside the autosampler. If the boats were pretreated in the muffle furnace, place boats on the tray in each of the 10 positions.
 - Tweezers must be used when handling the boats.
 - Close the cover to the autosampler when not actively adding or removing trays.
 - Place the sample tray on a clean surface, such as aluminum foil or paper, to prevent contamination.
3. Place the second sample boat on the balance and tare
 - The first boat is used as a conditioning blank.
4. Set up the sample table (right tab in MA3Win). The first position is the conditioning blank; positions 2, 3 and 4 are set for the QC sample. Samples are added to the table in triplicate.
5. In the “METHOD NUMBER” column, select the catalyst method as described in Table 2 above.
6. In the sample size (SVOL [mg]) column of the first QC sample, right click and select the option “Balance Volume Set” to enable direct transfer of the sample mass from the balance into WA3Win.

- Alternatively, sample mass can be typed directly into the table, but the direct communication from the balance minimizes transcription errors.
7. Carefully transfer approximately 50 mg of sample into the boat with a disposable transfer pipet, or approximately 50 μL if using a digital pipet, and press the print button to transfer the sample size from the balance into MA3Win.
 8. Repeat until all sample boats in the tray have been loaded. Continue with additional trays as needed.
 - It is a good practice to analyze a QC standard in the beginning of the run before the first sample to ensure that the equipment is functioning properly. After the first sample tray, load 3 samples in triplicate with the last position reserved for the QC standard.
 - Triplicate analysis is recommended to prevent any sample inhomogeneity from affecting the results.
 9. Click the “MEASURE” box in the left column next to each sample to be analyzed then click the “START” icon to begin the analysis. The analysis will proceed automatically until the final sample has been measured.

Calculations

All calculations are performed by the MA3Win software. Results below 10 ppb are reported to 1 decimal place; samples 10 ppb and higher are typically reported as whole numbers. Samples are reported by the software as ng/g (mass-ppb) or $\mu\text{g/g}$ (mass-ppm).

Precision

Precision statements were determined using UOP Method 999, “Precision Statements in UOP Methods”.

A nested design was carried out for mercury in solids analysis with two analysts. Each analyst carried out tests on two separate days, performing two tests each day using two samples. The total number of tests performed was 8 for each component. Using a stepwise analysis of variance procedure, the within-day and within-lab estimated standard deviations (esd) were calculated for the components at the concentration levels listed in Table 4. Two tests performed 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 tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 5 with 95% confidence.

The data in Table 4 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.

Repeatability and Site Precision

Table 4
Repeatability and Site Precision, ng/g (mass-ppb) or $\mu\text{g/g}$ (mass-ppm)

<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>
Fly Ash (NBS 1633)	132 ppb	2.2	9	2.9	11
Catalyst	38 ppb	1.0	4	1.5	7
Regenerated Catalyst	1.4 ppb	0.10	0.4	0.15	0.6
Spent Catalyst	58 ppm	1.0	4	1.1	4

Reproducibility

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

Time for Analysis

The elapsed time for calibration is approximately 3 hours. The labor requirement is 0.5 hours. Once calibrated, analysis of a single sample requires 0.5 hours of labor (including grinding) and approximately 1 hour of elapsed time. These times do not include instrument warm up time or the preparation of boats.

Suggested Suppliers

Airgas USA, LLC, 259 North Radnor-Chester Rd., Suite 100, Radnor, PA 19087-5283 (610-687-5253), www.airgas.com

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300) www.fishersci.com

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

Nippon Instruments North America, 1511 Texas Ave. South, #270 College Station, Texas 77840 (979-774-3800), www.hg-nic.us US distributor for Nippon Instruments Corp., 14-8 Akaoji-cho, Takatsuki-shi, Osaka, 569 Japan (0726 94-5195) (Fax 0726-94-0663) www.hg-nic.com

NIST Office of Reference Materials, 100 Bureau Drive, Stop 2300, Gaithersburg, MD 20899-2300 (301- 975-2200) www.nist.gov

o2si smart solutions, PO Box 30712, Charleston, SC 29417 (843-763-4884) www.o2si.com

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

Sigma-Aldrich, P.O. Box 355, Milwaukee, WI 53201 (414-273-3850) www.sigma-aldrich.com

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