Honeywell
UOP

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).

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:

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

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)
$\mathbf{10^3}$ = 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**