



Total Mercury Analysis in Liquefied Petroleum Gases

UOP Method 1033-19

Scope

This method is for determining the total mercury concentration in liquefied petroleum gases, using a Nippon Instrument Corporation (NIC) WA-5F mercury analyzer with a NIC LP-WA vaporizer and dry gas meter (DCDa-1C) with a lower limit of quantification of 0.1 mass ppb. Mercury is trapped in a gold trap, released using heat, and quantified using atomic fluorescence spectroscopy (AFS).

References

ASTM Method D6350, "Standard Test Method for Mercury Sampling and Analysis in Natural Gas by Atomic Fluorescence Spectroscopy," www.astm.org

UOP Method 516, "Sampling of Gasolines, Distillate Fuels and C₂-C₄ Fractions," www.astm.org

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

Outline of Method

The NIC WA-5F mercury analyzer with a dry gas meter is specified for this method. LPG can be directly sampled using the LP-WA vaporizer from a Sulfinert™ coated cylinder. The sample is passed over a mercury collector tube. Re-purification then occurs by heating to release the mercury and trapping on a second mercury collector as a gold amalgam. The second mercury collector is heated under Argon gas flow and analyzed in the AFS cell.

Apparatus

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

Cylinder, collection, for sample collection from process stream, stainless steel, Sulfinert™ coated, 1000-mL, with valve and valve with outage tube, Restek, Cat. Nos. 24134, 21400, and 21402-038, respectively. (See Note)

Cylinders, graduated, borosilicate glass, 50-, 100- and 250-mL, Fisher Scientific, Cat. Nos. 08-556C, D and E, respectively

Flasks, volumetric, 1000-mL, with caps, Fisher Scientific, Cat. No. 10-210-5G. Several are required, see *Reagents and Materials* and *Procedure*.

Gage, pressure, 0-20,000 kPa gage (0-3000 psig), 2-inch diameter, ¼"-inch MNPT, used for testing the pressure of an unknown LPG sample gas cylinder, Matheson Gas Products, Model 63-2233

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 THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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Mercury AFS analyzer, with attached vaporizer, dry gas meter, and computer. This method was developed and validated using the Nippon Instrument Corporation WA-5F mercury analyzer, with LP-WA heated vaporizer and DCDA-1C dry gas meter. The procedure for analysis may be different for other instruments and all other instruments need to be validated before using this method.

Mercury collector tube, M-160, Nippon Instrument Corporation

Mercury Vapor Calibration Box, MB-1, Nippon Instrument Corporation

Oven, drying, capable of maintaining 105°C

Syringe, Gastight, Hamilton 1700 series, 100 µL volume with side port needle, VWR, Cat. No. 60376-528

Regulator, inert gas, two-stage, Matheson Tri-Gas, Models 3810A-580

Reagents and Materials

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

Acetone, certified, Burdick & Jackson, Cat. No. AH010-4PC

Argon, ultra-high purity grade, 99.999%, local supply

Ice, water

Isooctane, certified, Burdick & Jackson, Cat. No. 362-1L

Isooctane-acetone, 9 to 1, Measure 900 mL of isooctane into a 1000-mL volumetric flask and fill with acetone to the mark. Cap and mix thoroughly by inverting at least ten times.

Kimwipe®, Kimberly-Clark® delicate task wipers, Fisher Scientific, Cat. No. 06-666A

Methanol, certified, Burdick & Jackson, Cat. No. AH230-4PC

Methanol-acetone, 1 to 1. Measure 500 mL of acetone with a graduated cylinder into a 1000-mL volumetric flask and fill to the mark with methanol. Cap the flask and mix by inverting at least ten times.

Phosphate buffer solution, pH 6.86 at 25 °C, 500 mL, local supply

pH paper, CF strips, 0 to 14 pH units, Fisher Scientific, Cat. No. 09-876-17

Sulfuric acid, reagent grade, ACS, 95.5%, Fisher Scientific, Cat. No. A300-212

Sulfuric acid, 10%. Prepare one liter by slowly adding 100 mL of concentrated sulfuric acid from a graduated cylinder to approximately 800 mL of water in a 1000-mL volumetric flask while cooling in ice water. After the heat of dilution dissipates, dilute to volume with water. Mix thoroughly by capping the flask and inverting at least 10 times.

Teflon-tape, PTFE, roll, 12.5-mm (0.5-inch), Fisher Scientific, Cat. No. 14-610-120

Water, deionized or distilled

Procedure

The analyst is expected to be familiar with general laboratory techniques, mercury analysis, and the equipment being used. Dispose of used reagents, materials, and samples in an environmentally safe manner according to local regulations.

Cylinder Preparation

1. Clean the interior surfaces of the 1000-mL extraction cylinder and valves as follows: Rinse the cylinder with 100 mL of the isooctane-acetone mixture and follow with a 100 mL rinse of the methanol-acetone mixture. Repeat until the rinse is colorless. Rinse with 100 mL the 10% sulfuric acid solution. Rinse with water until the rinse is neutral to the pH paper. Appropriately discard the washers.
 - If any of the rinses are colored or dirty upon draining, repeat that rinse until the drained material is clear.
2. Remove the water by rinsing the cylinder and valves with two successive 100 mL aliquots of the methanol-acetone mixture and discard the rinses.
3. Flush the cylinder with nitrogen to remove any remaining solvents. Dry in a drying oven for at least one hour at 105 °C.
4. Allow the cylinder to cool to room temperature.

Sample Collection

Samples must be initially collected, in accordance with UOP Method 516, "Sampling of Gasolines, Distillate Fuels and C₂-C₄ Fractions," in a coated cylinder to prevent loss of mercury to the cylinder walls.

Instrument Set Up

Start the instrument and prepare per the manufacturer's recommendations. Wait a minimum of 20 minutes after the instrument is turned on to allow it to stabilize. During this time, conduct the equipment check and follow the instructions in the WA5FWin Software. Prior to use, ensure that there is approximately 1 inch of the phosphate buffer solution in the trap to scrub potential contaminants from entering the instrument. The standard operating conditions for this method can be found in Table 1.

Table 1
Operating Conditions

Light source	Low pressure mercury discharge tube
Detector	Photoelectric tube
Detection Wavelength	253.7 nm
Carrier gas	Purified Air/Argon
Flow rate	0.5 L/min
Collector tube set temp	600 °C
Collection tube heat time	180 sec
Purge 1 time	10 sec
Purge 2 time	60 sec
Measure delay	5 sec
Measure time	30 sec
Cool down	30 sec

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 steps to calibrate the instrument are described below. Hg vapor volumes of 30, 60, and 90 µL are recommended for the calibration. A recheck standard sample should be used at the start of a run after initial calibration to ensure the calibration still holds. All of the following steps should be conducted

in an operating fume hood ensuring appropriate PPE is used. Figures 1 and 2 show the representative time-resolved fluorescence spectrum and an example of the calibration curve.

1. Perform a blank run by entering a value of 0 μL mercury in the standard one position in the WA5FWin software and clicking the start button. Enter values of 30, 60, and 90 μL for the remaining standards along with the temperature of the Hg vapor box (assuming a lab temperature of approximately 22.5 $^{\circ}\text{C}$, the highest standard will be about 1.5 ng Hg)
2. Clean the tip of a gas-tight 100 μL syringe with a Kimwipe® and insert the needle into the septum of the Hg gas box (see note 1).
3. Prime the syringe by lifting past the desired volume three times. On the fourth time pull past the desired volume and remove the syringe from the Hg gas box.
4. Wipe the needle with a Kimwipe®, then with the needle pointing up (since Hg is more dense than air, any air will rise to the top of the syringe) press the plunger until a volume of 30 μL is reached.
5. When the instrument is in the “Trans” phase of the 30 μL standard, insert the needle into the septum of the instrument and inject the Hg vapor. The injection should be completed as early in the 3 minute window as possible.
6. Repeat steps 2-5 with volumes of 60 and 90 μL of Hg vapor. Confirm a linear calibration.

Sample Analysis

All steps should be completed using appropriate PPE and in a properly functioning fume hood.

1. At the start of each run, run a recheck standard noting the temperature of the Hg vapor box and follow with a blank. The time on the sample tab for all recheck standards and blanks should always be 0 min. Follow steps 2-5 in the “Calibration” section to complete a recheck standard.
2. Open the liquid valve on the sample cylinder briefly to push a small amount of gas out of the cylinder to remove any dust particles that may be present on the port.
3. Connect the liquid sampling side of your sample cylinder to the LP-WA connection port using the appropriate wrenches to tighten. Do not overtighten the connection or exert excessive strain on the LP-WA port (see Figure 1). Ensure that the pressure valve on the LP-WA is fully loosened (counter-clockwise).
4. Open the valve on the sample cylinder, then slowly turn the knob on the LP-WA until the pressure reads 0.02 MPa (do not exceed 0.05 MPa, if you go past 0.02, do not turn the knob back in the other direction).
5. Insert sample information into the samples tab of the WA5FWin software (see Figure 2) and select 1 minute for initial sampling (this will sample approximately 0.5 L of gas). Always start with 1 minute sampling time to avoid exposing the collector tube to large amounts of mercury that could be present in the unknown sample.
6. Click start button in the WA5FWin software and click yes on the pop-up for initial gas purge. This feature will add a line on the sample list and sample for 1 minute to ensure other gas is not present in the lines.
7. If the quantity of mercury detected is lower than 0.15 ng, it is recommended to increase the sampling duration to ensure optimal accuracy of the measurement (suggested progression is 2 minutes then 4 minutes). If all measurements are required, an estimate of 4 L of gaseous sample would be required. Alternatively, a calibration curve with lower mercury concentrations could be generated.

8. After sample analysis is completed, close the valve on the sample cylinder. In the WA5FWin software, click the “Exh” button to exhaust any remaining gas from the lines. After the pop-up in the software saying the exhaust step is complete, turn the pressure valve on the LP-WA fully counter-clockwise. Disconnect the sample cylinder from the LP-WA. Proceed to the next sample or run a check standard, followed by a blank prior to instrument shutdown.

Calculations

Initial calculations are performed by the WA5FWin software. Results for Hg concentrations in the analyzed gas are expressed as $\mu\text{g}/\text{m}^3\text{N}$. The N refers to a normalization factor (set to 0 °C in software) to account for potential variations in gas sampling. This can be converted to mass-ppb in the LPG for a known composition sample through the following equation 1. If the sample composition is unknown, conversion to mass-ppb ($\mu\text{g}/\text{kg}$) cannot be completed.

$$\text{Concentration of mercury in LPG, } \mu\text{g}/\text{kg} = \frac{C}{M} \quad (1)$$

where:

C = concentration of mercury determined by instrument, $\mu\text{g}/\text{m}^3$

M = mass of LPG in 1 L of gas, kg/m^3

To calculate the mass of LPG in 1L, use equation 2:

$$\text{Mass of LPG in 1 L, } \text{kg}/\text{m}^3 = \frac{MW}{22.7} \quad (2)$$

where:

MW = molecular weight of LPG, g/mol

22.7 = volume of gas for 1 mole at standard pressure and 0 °C, L/mol

Table 2 shows the conversion factor for a few hydrocarbons between $\mu\text{g}/\text{m}^3$ and mass-ppb. The conversion factor for blends of known composition can be calculated by proportionately weighting individual component's factors.

Table 2	
<u>Conversion factors for common LPG</u>	
<u>Matrix</u>	<u>Conversion factor from $\mu\text{g}/\text{m}^3$ to mass-ppb</u>
Propane	0.5149
Propylene	0.5394
Butane	0.3906

Notes

1. Stability of Hg in the cylinder has been shown to be good by the manufacturer and internal testing, but it is suggested that turnaround time between sampling and analysis be minimized.
2. Be sure to note the temperature of the Hg gas box when each standard is collected and change the temperature in the WA5FWin software if needed. This will automatically calculate the amount of Hg for the calibration curve.

Precision

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

Repeatability and Site Precision

A nested design was carried out for mercury in LPG analysis with two analysts. Each analyst carried out tests on two separate days, performing two tests each day using two LPG spikes. During sampling of propylene, an injection of 0.4530 ng Hg was made through the injection port on the instrument. The total number of tests performed was 8. Using a stepwise analysis of variance procedure, the within-day and within-lab estimated standard deviations (esd) were calculated for the components at the concentrations listed in Table 3. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 2 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 2 with 95% confidence.

Table 3

Repeatability and Site Precision, ng

<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>
0.4530	0.001	0.007	0.005	0.031

For the 1, 2, and 4 minute sampling times recommended, assuming a flow rate of approximately 0.5 L/min, the summary of the precision data expressed as $\mu\text{g}/\text{m}^3$ are shown in Table 4.

Table 4

Repeatability and Site Precision, $\mu\text{g}/\text{m}^3$

<u>Sampling Time</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>
1 min	0.002	0.014	0.01	0.062
2 min	0.001	0.007	0.005	0.031
4 min	0.0005	0.0035	0.0025	0.0155

The data in Tables 3 and 4 represent short-term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of long-term repeatability.

Reproducibility

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

Time for Analysis

The elapsed time for calibration is approximately 1 hour. The labor requirement is 0.5 hours. Once calibrated, analysis of a single sample requires 0.25 elapsed time and labor time at higher concentrations. Low concentration samples may require up to 1 hour of analysis. These times do not include instrument warm up.

Suggested Suppliers

Burdick & Jackson, 1953 S. Harvey St., Muskegon, MI 49442, USA, 1-973-455-5268,
www.bandj.com

Fisher Scientific, 300 Industry Dr., Pittsburgh, PA 15275, USA, 1-412-490-8300,
www.fishersci.com

Matheson Tri Gas, 150 Allen Rd # 302, Basking Ridge, NJ 07920, USA, 1-908-991-9200,
www.mathesontrigas.com

Nippon Instruments North America, 1511 Texas Ave. South, #270 College Station, TX 77840,
USA, 1-979-774-3800, 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

Restek, 110 Benner Circle, Bellefonte, PA 16823, USA, 1-814-353-1300, www.restek.com

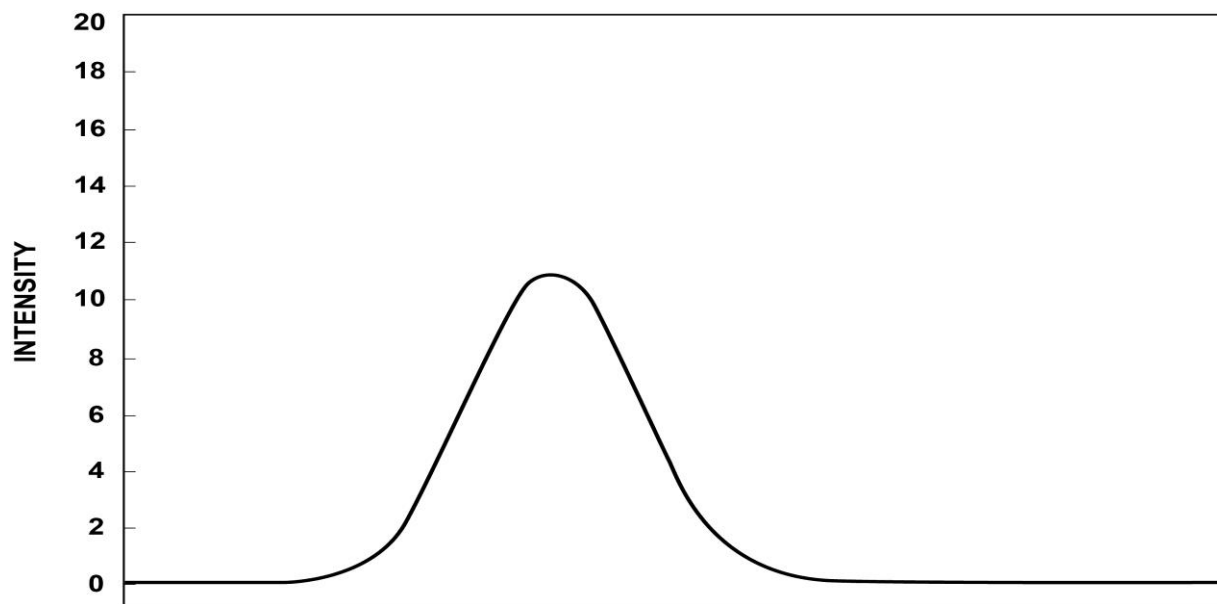


Figure 1
Time resolved fluorescence spectrum of Hg in LPG

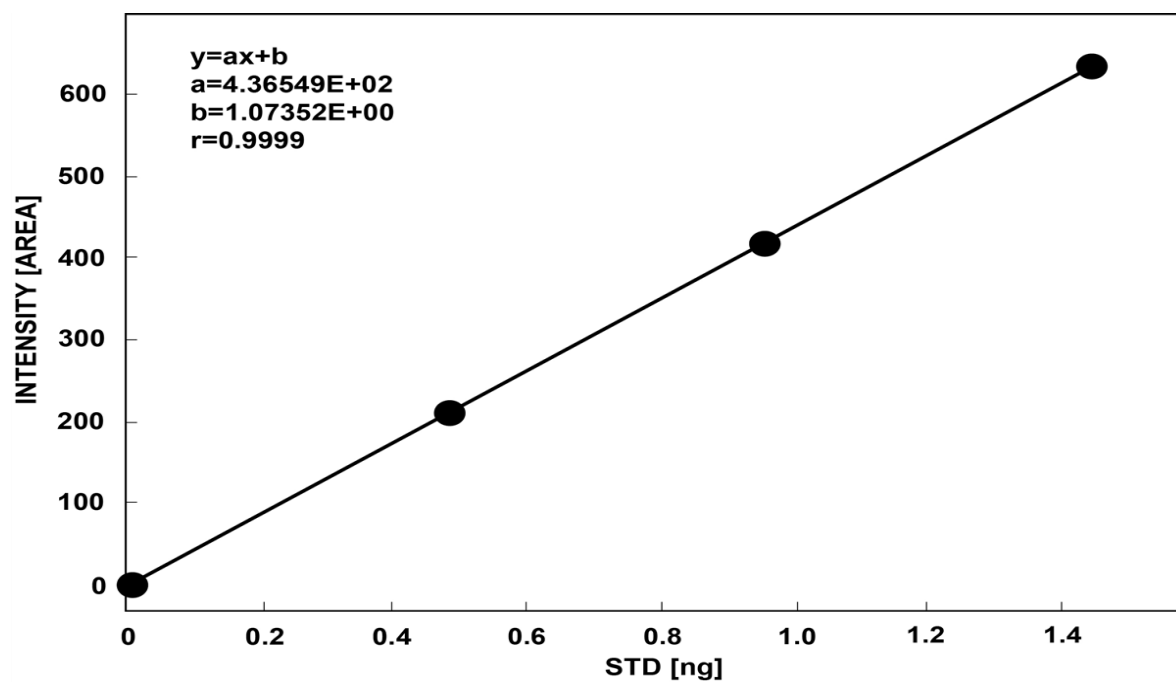


Figure 2
Calibration curve of Hg on WA-5F analyzer