



A Honeywell Company

Free Sulfur in LPG by Mercury Number

UOP Method 377-13

Scope

This is a semi-quantitative method for determining free sulfur in liquefied petroleum gases. Peroxide is an interference that increases the apparent elemental sulfur value. The lower limit of detection is a mercury number of 1.0, which is equivalent to approximately 2.0 mg/kg (mass-ppm).

References

ASTM Method D1657, "Density or Relative Density of Light Hydrocarbons by Pressure Hydrometer," www.astm.org

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

Outline of Method

A known mass of liquefied petroleum gas (LPG) is dissolved in toluene and then the LPG is evaporated. The remaining toluene, which contains the elemental sulfur, is placed in a bottle to which oleic acid and mercury are added and the mixture is shaken vigorously. The resulting mercuric sulfide suspension is visually compared to a set of previously prepared standards containing known amounts of elemental sulfur. A relative density of the LPG is determined and the mercury number is calculated. The sulfur concentration can also be calculated in mass-ppm.

Definition

Mercury Number is defined as milligrams of free sulfur per liter.

Apparatus

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

Balance, 8000-g capacity, readable to 0.1 g

Balance, readable to 0.0001 g

Bottles, clear oil sample, 118-mL, with cork stopper, Fisher Scientific, Cat. No. 02-911-472. Mark each bottle at the 100-mL point by filling the bottle with a measured 100 mL of water, and marking with a marker or scribe.

Cylinders, graduated, 5- and 50-mL, Fisher Scientific, Cat. Nos. 08-550A and -550D, respectively

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Delivery tube, stainless steel, 6.35-mm OD, for LPG sample cylinder, 100-mm length with a connection on one end that corresponds with the outlet connection of the sample cylinder and the other end plain.

Flask, Erlenmeyer, 500-mL, Fisher Scientific, Cat. No. FB-500-500

Flask, volumetric, 1000-mL, Fisher Scientific, Cat. No. 10-212-5L

Hood, laboratory fume

Marker, diamond point, Fisher Scientific, Cat. No. 75-0

Pipet, Mohr, 1-mL, 0.1-mL sub-divisions, Fisher Scientific, Cat. No. 13-665-G

Pipets, volumetric, Class A, 2- and 100-mL, Fisher Scientific, Cat. Nos. 13-650-2C and -2U, respectively

Timer, laboratory, Fisher Scientific, Cat. No. 14-648-35

Reagents and Materials

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

Boiling chips, carbon, Fisher Scientific, Cat. No. 09-191-12

Mercury, triple distilled, Fisher Scientific, Cat. No. 7439-97-6

Oleic acid, Fisher Scientific, Cat. No. A195

Sulfur, precipitated, Fisher Scientific, Cat. No. 7704-34-9. Flowers of sulfur cannot be used.

Toluene, 99.8% minimum purity, Fisher Scientific, Cat. No. 108-88-3

Procedure

The analyst is expected to be familiar with general laboratory practices and the equipment being used. Dispose of used reagents, materials, and samples in an environmentally safe manner according to local regulations. Perform all activities except weighing in a laboratory hood.

Preparation of Standards

Prepare a standard sulfur stock solution as follows:

1. Place $1.0 \text{ g} \pm 0.001 \text{ g}$ of precipitated sulfur in a 1000-mL volumetric flask.
 - Do not use flowers of sulfur.
2. Add toluene to dissolve the sulfur.
3. Fill to the mark with toluene and shake to mix.
 - This standard sulfur stock solution contains 1.0 mg of elemental sulfur per mL.

Standard Mercuric Sulfide Suspensions

1. Add by pipet 100 mL of toluene and 2 mL of oleic acid into each of 10 clear oil sample bottles.
 - The oleic acid is added as a dispersant for the mercuric sulfide formed.
2. Add measured amounts of the standard sulfur solution with a 1-mL Mohr pipet to produce a series of standards containing from 0.1 to 1.0 mg of elemental sulfur per 100 mL in 0.1-mg increments.

- For example, add 0.1 mL to the first bottle, 0.2 mL to the second bottle and so forth.
3. Add with a graduated cylinder 3 mL of clean mercury to each sample bottle, stopper and shake for 3 minutes.
 - Prepare new standards at weekly intervals.
 - Caution: Take suitable precautions to avoid contact with mercury or mercury vapors, including, but not limited to, conducting operations in an approved fume hood.

Determination of Free Sulfur

1. Add with a graduated cylinder 50 mL of toluene to a 500-mL Erlenmeyer flask.
2. Attach the delivery tube to the cylinder containing the LPG sample.
3. Weigh the sample cylinder assembly to the nearest 0.1 g.
4. Position the cylinder so the tip of the delivery tube is completely immersed in the toluene.
5. Open the cylinder valve to transfer 200 to 300 mL of the LPG into the flask.
 - The transfer is made as rapidly as possible without splattering the contents of the flask.
 - The transfer is made at room temperature.
 - The purpose of rapid sampling is to keep the sample substantially liquid and to wash into the flask any sulfur that might crystallize in the delivery tube.
6. Re-weigh the sample cylinder assembly to the nearest 0.1 g.
 - The sample mass taken for analysis is the difference in mass of the sample cylinder assembly before and after sampling.
7. Allow the LPG to boil off at room temperature in a fume hood.
8. Transfer the toluene solution to the oil sample bottle.
9. Rinse the flask 3 times with 10-mL aliquots of the toluene and add these rinsings to the oil sample bottle.
10. Adjust the total volume of toluene in the sample bottle to 100 mL.
 - The sample bottle is previously marked at 100 mL by calibration with water.
11. Add by pipet 2 mL of oleic acid.
12. Add with a graduated cylinder 3 mL of mercury.
13. Stopper and vigorously shake for 3 minutes.
14. Compare the color intensity of the suspension in the unknown sample to the set of freshly shaken standards using any source of transmitted light and choose the standard that most closely matches the unknown sample.
 - If the sample is darker than the standard containing 1.0-mg sulfur per 100-mL, repeat the determination, taking a smaller sample, to obtain a match within the range of the standards.
15. Determine the relative density of the sample by ASTM Method D1657, "Density or Relative Density of Light Hydrocarbons by Pressure Hydrometer," if a mercury number is to be reported.

Calculations

Calculate the mercury number of the sample to one decimal place using Equation 1:

$$\text{Mercury number} = \frac{1000 H S}{G} \quad (1)$$

where:

G = sample mass, g
H = mass of sulfur in matching standard, mg
S = relative density of the sample
1000 = factor to convert mL to L

Calculate the mass-ppm concentration of free sulfur in the sample to one decimal place using Equation 2:

$$\text{Free Sulfur, mass-ppm} = \frac{1000 H}{G} \quad (2)$$

where:

G, H, and 1000 = previously defined, Equation 1

Note

The presence of hydrogen sulfide is not an interference.

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 determining free sulfur on one sample. The sample was analyzed by two analysts, with each analyst performing two analyses on two separate days for a total of eight analyses. Using a stepwise analysis of variance procedure, the within-day and within-lab estimated standard deviations (esd) were calculated at the concentration means listed in the Table. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in the Table with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in the Table with 95% confidence.

Table
Repeatability and Site Precision

<u>Value</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>
Mercury number	2.3	0.18	0.7	0.23	1.4
mg/kg (mass-ppm)	4.0	0.30	1.2	0.40	2.4

The data in the Table 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 are 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 one analysis, not including preparation of standards, is 0.75 hour. The labor requirement is 0.5 hour.

Suggested Supplier

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785, USA, 1-412-490-8300,
www.fishersci.com