



A Honeywell Company

Trace Sulfur in LPG and Gaseous Hydrocarbons by Oxidative Combustion with Ultraviolet Fluorescence Detection

UOP Method 989-14

Scope

This method is for determining sulfur in liquefied petroleum gas (LPG) and gaseous hydrocarbons at concentrations ranging from 0.2 to 100 mg/kg (mass-ppm).

LPG samples are expanded into the gas phase before analysis. If any heavy sulfur compounds are present in the LPG that do not volatilize quantitatively with the LPG, they may be under-reported. The method can also be applied to the analysis of hydrogen and other gas samples. Halogens interfere at concentrations greater than approximately 0.3%.

This method is similar to ASTM Method D6667, "Total Volatile Sulfur in Gaseous Hydrocarbons and Liquefied Petroleum Gases by Ultraviolet Fluorescence," and ASTM Method D7551, "Total Volatile Sulfur in Gaseous Hydrocarbons and Liquefied Petroleum Gases and Natural Gas by Ultraviolet Fluorescence," but uses a different sample introduction system which may improve precision and accuracy.

References

ASTM Method D6667, "Total Volatile Sulfur in Gaseous Hydrocarbons and Liquefied Petroleum Gases by Ultraviolet Fluorescence" www.astm.org

ASTM Method D7551, "Total Volatile Sulfur in Gaseous Hydrocarbons and Liquefied Petroleum Gases and Natural Gas by Ultraviolet Fluorescence," www.astm.org

UOP Method 516, "Sampling and Handling of Gasolines, Distillate Fuels and C₃-C₄ Fractions," www.astm.org

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

Outline of Method

A commercial instrument is set up and calibrated with different volumes of LPG standards. The gas or LPG materials are dispensed into fluoropolymer gas sampling bags and, if LPG, are allowed to evaporate. The atmospheric pressure gas sample is injected into an argon carrier flow using a syringe-based gas injector. The gas mixture is combined with oxygen at high temperature. The organic material is converted to carbon dioxide and water. The sulfur in the sample is converted to sulfur dioxide. The signal is proportional to the total volatile sulfur in the sample.

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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Nonconfidential UOP Methods are available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, USA. The UOP Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Apparatus

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

Regulator, argon, single-stage, with stainless steel diaphragm, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Cat. No. 3231. This regulator is installed downstream of the two-stage regulator to provide better flow control.

Regulator, argon, two-stage, with stainless steel diaphragm, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Cat. No. 3122-580

Regulator, oxygen, single-stage, with stainless steel diaphragm, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Cat. No. 3231. This regulator is installed downstream of the two-stage regulator to provide better flow control.

Regulator, oxygen, two-stage, with stainless steel diaphragm, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Cat. No. 3122-540

Sulfur analyzer, with attached furnace, autosampler, controls and computer, Model TS-100V, with SD-100 Sulfur Detector and GI-220 Gas Injector, Mitsubishi Chemical Analytech, available from COSA Instrument. This method was developed and validated using the Mitsubishi analyzer. The procedure for analysis may be different for other instruments and other instruments need to be validated before using for this method. Not all combustion/UV fluorescence instruments are capable of running this analysis. The Mitsubishi analyzer must be equipped with the following accessories:

Gas Injector, Mitsubishi GI-220, COSA Instruments

Membrane drier, Perma Pure MD-110-24F-4 or Tube Dryer, Mitsubishi, Cat. No. TN6RPC, COSA Instruments (see *Note 1*)

Reagents and Materials

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

The following items are required to perform the analysis. Additional reagents and materials may be required depending on the specific instrument.

Air, compressed, dry, oil-free, for membrane drier (if the instrument does not purge the drier with argon), local supply

Alumina balls, Mitsubishi, Cat. No. TS3CAT, COSA Instruments

Argon, compressed gas, 99.99% minimum purity, UHP, Matheson Tri-Gas or local supply

Gas sampling bags, 1.6-L or 3.8-L, Cat. No. 10-923-10 or -11, Fisher Scientific (see *Note 2*)

LPG standards, 1.5, 15, 75, and 150 mass-ppm methyl mercaptan (methanethiol) in n-butane, Matheson Tri-Gas

Oxygen, compressed gas, 99.98% minimum purity, UHP, Matheson Tri-Gas or local supply

Quartz wool, Mitsubishi, Cat. No. TNQWL, COSA Instruments

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of sulfur

analysis using ultraviolet fluorescence, and the equipment being used. Dispose of used supplies and samples in an environmentally safe manner according to applicable regulations.

Preparation of Standards

The calibration standard of methylmercaptan in n-butane is purchased as a certified standard from gas suppliers. A 1.5 mass-ppm methylmercaptan in n-butane standard is 1.0 mass-ppm S. When expanded to atmospheric pressure in the gas sampling bag, it contains 2.592 ng/mL (as S) at 0 °C or 2.375 ng/mL (as S) at 25 °C. Calculate the gaseous sulfur concentration in the vaporized standard from the concentration of the methylmercaptan in n-butane LPG standard using Equation 1.

$$A = 1.728 C \left(\frac{273.15}{T} \right) \quad (1)$$

where:

A = gaseous sulfur concentration of the vaporized standard, at specific temperature, ng/mL

C = concentration of methylmercaptan in LPG blend, µg methylmercaptan/g of LPG (mass-ppm)

T = absolute temperature, K

$$1.728 = \left(\frac{32.064}{48.107} \right) \left(\frac{58.124}{22.414} \right) \quad (1a)$$

where:

32.064 = atomic mass of S, g/mol

48.107 = molecular mass of methylmercaptan, g/mol

58.124 = molecular mass of butane, g/mol

22.414 = volume of ideal gas at STP, L/mol

Calculate the mass of sulfur injected from the injection volume and the gaseous sulfur concentration using Equation 2.

$$B = A V \quad (2)$$

where:

A = previously defined, Equation 1

B = mass of injected sulfur, ng

V = gaseous volume of expanded calibration blend injected, mL

Sampling

The sample should be collected according to UOP Method 516, "Sampling and Handling of Gasolines, Distillate Fuels and C₃-C₄ Fractions." The use of a passivated cylinder (e.g. Silcosteel™, Sulfinert™, etc.) is required (see *Note 3*). The transfer of the LPG or gas sample to the gas sampling bag should be performed in a fume hood. A new bag should be used for each sample to prevent contamination.

1. Flush the sample cylinder outlet with sample for a few seconds before connecting to the gas sampling bag.
2. Open the valve on the gas sampling bag.
3. Open the cylinder valve briefly, allowing sample to flow into the bag. Do not overfill the bag.
 - For LPG samples, transfer a small volume of LPG (2 - 4 mL) and allow it to vaporize (this is for a 1.6-L bag; approximately twice that amount for a 3.2-L bag).
 - For gas samples, fill until the bag expands, but is not completely full.

4. Close the valve on the gas sampling bag and remove from the cylinder.
5. Analyze the sample within two hours of transferring to the gas sampling bag.

Preparation of Apparatus

Set up the instrument according to the manufacturer's instructions. Connect the membrane drier in series between the combustion tube and the detector. Allow the instrument to warm up and the baseline to stabilize before injecting samples. Suggested Operating Conditions for the Mitsubishi TS-100V analyzer are listed in Table 1. A 25-mL syringe is installed in the GI-220 gas injector.

Table 1
Operating Conditions for Mitsubishi TS-100V/SD-100/TRU-100

Upper temperature ^a	900 °C
Lower temperature ^b	1000 °C
Argon main	170 mL/min
Oxygen main	150 mL/min
Argon auxiliary	50 mL/min
Oxygen auxiliary	400 mL/min
GI-220 carrier argon	80 mL/min
Gain	Middle
Normal end	Off
Minimum area	40000
Baseline	75%
GI-220 Syringe	25 mL
Absorption rate	50 mL/min
Injection rate	20 mL/min
^a Combustion tube, upper portion	
^b Combustion tube, lower portion	

Calibration

Calibrate weekly when in use. Check the calibration daily when in use, by analyzing one of the calibration standards or a reference material. If the results deviate from the known concentration by more than the repeatability allowable difference shown in *Precision*, recalibrate.

1. Transfer the calibration standard to a gas sampling bag, and then connect to the GI-220 gas injector module.
 - The same gas sampling bag can be re-used for the standard. Empty the bag before refilling.
2. Set up the sample table for multiple sample volumes and replicate injections of the sulfur standard. Three or four injections are recommended.
3. Analyze the standard according to the instrument manufacturer's instructions.
 - If run as a "calibration" method, the "START" button will need to be pressed for each new sample volume. If run as a "sample" method, the instrument will run all measurements on the same material automatically, and the S content and response areas can be entered in manually (see *Note 4*).
 - Relative standard deviation (RSD), as calculated by the instrument for the standards, should be within 15% for the 1- or 2-mL injections and within 10% for 3-mL or larger injections.
4. Create a regression line using the instrument software and the appropriate volumes of the standards. Set the regression line to "y=bx+c" for this calibration.

Sample Analysis

1. Determine the average molecular weight of the sample, see the *Appendix*.

2. Attach the gas sampling bag with the first sample to the GI-220 gas injector module.
3. Add the sample to the sample table. Set the sample injection volume to 5 mL.
 - If unsure of concentration, start with a 1-mL sample volume to avoid overloading the system.
 - Analyze samples above 5 mg/kg in duplicate. For samples below 5 mg/kg, three or more measurements should be made.
 - Enter the sample average molecular weight to calculate the results as mass-ppm.
4. Analyze the sample replicates according to the instrument manufacturer's instructions.
5. Repeat Steps 1 through 4 for each additional sample.
 - If the detector becomes contaminated (trace off scale), disconnect the gas sampling bag and analyze air blanks until the response stabilizes. Then confirm that the sensitivity has not changed by analyzing a calibration standard or a control standard.
 - Integration and calculations are done automatically. The average of the replicate injections is calculated by the instrument software.

Calculations

All calculations are performed by the software and results are displayed and printed in mass-ppm (mg/kg). The molecular weight of the sample is input during sample data entry and is used by the instrument to convert results from mass/volume to mass/mass.

- Multiple injections of the same sample are averaged by the instrument software.

Report

Report results as mg/kg (mass-ppm) to one decimal place below 10 mg/kg and the nearest whole number above 10 mg/kg.

Notes and Precautions

1. The membrane drier is used to remove the water produced during combustion. If not removed, the water vapor can react with the sulfur dioxide to form H_2SO_3 with a resultant loss of signal. The membrane drier consists of a thin walled Nafion™ tube within a larger plastic tube. The combustion product gas flows through the Nafion tube. Dry air or other dry gas flows counter-current through the outer plastic tube. The Nafion membrane allows water to pass through, and be carried away by the air stream on the other side.
2. Gas sampling bags are made of Tedlar™ or other fluoropolymers. The fitting on the gas sampling bags may not match the connector on the GI-220. In that case, an adapter, such as a short section of silicone tubing, should be used to make the connection. Samples should be analyzed within two hours of transfer into the gas sampling bag.
3. The use of passivated cylinders (e.g. Silcosteel, Sulfinert, etc.) is required to prevent the loss of sulfur compounds to the cylinder wall. The internal components of the cylinder valves should be similarly treated.
4. When running the calibration as "samples," type in the calibration data manually to create a calibration. Run the sample report to print the individual measurements. Calculate the sulfur content for each injection volume using the equations in "Preparation of Standards." Under the "System" menu, select "Default Calibration Curve." Click "Edit" and enter all of the calibration data points. Save the calibration.

Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods." As described in the *Procedure* and *Calculations*, two to four replicate injections were averaged for each analysis.

Repeatability and Site Precision

A nested design was carried out for determining impurities in three LPG samples and one gas sample by two analysts on two separate days, performing two analyses each day for a total of 32 analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table 2. 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 Table 2 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 Table 2 with 95% confidence.

Table 2
Repeatability and Site Precision, mg/kg

<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>
LPG 1	1.0	0.02	0.1	0.03	0.1
LPG 2	5.7	0.23	0.9	0.29	1.3
LPG 3	19.8	0.21	0.8	0.19	0.8
LPG 4	53.4	0.22	0.9	0.64	3.9

The data in Table 2 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 the calibration is approximately 4 hours. When performed as in "calibration" mode, then the labor requirement for calibration is identical to the elapsed time, 4 hours. In "sample" mode, the labor requirement is approximately 1 hour. Each sample analysis requires 0.5 hour for duplicate measurement.

Suggested Suppliers

COSA Instrument Corp., 55 Oak St., Norwood, NJ 07648, USA, 1-201-767-6600, distributor for Mitsubishi Chemical Analytech, 370 Enzo, Chigasaki, Kanagawa Pref., 253-0084, Japan, +81-467-86-3864, www.cosainstrument.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

Perma Pure Inc., 8 Executive Dr., Toms River, NJ 08754, USA, 1-732-244-0010, www.permapure.com

Appendix

Calculation of the Average Molecular Weight of a Gas

Scope

This appendix may be used to calculate the average molecular weight of a gaseous material from its known composition.

References

ASTM Method D2163, "Hydrocarbons in Liquefied Petroleum (LP) Gases and Propane/Propene Mixtures by Gas Chromatography," www.astm.org

UOP Method 373, "Composition of C₂ through C₅ Hydrocarbon Mixtures by GC," www.astm.org

UOP Method 539, "Refinery Gas Analysis by Gas Chromatography," www.astm.org

Calculations

If the composition of the material is not known, analyze it using the following test methods. Other similar methods may be used.

For gas samples: UOP Method 539, "Refinery Gas Analysis by Gas Chromatography"

For LPG samples: UOP Method 373, "Composition of C₂ through C₅ Hydrocarbon Mixtures by GC," or ASTM Method D2163, "Hydrocarbons in Liquefied Petroleum (LP) Gases and Propane/Propene Mixtures by Gas Chromatography"

Calculate the average molecular weight of the gas sample (after expansion if the sample was an LPG), from its known composition, using Equation A1.

$$M = \sum_{i=1}^n \frac{P_i W_i}{100} \quad (A1)$$

where:

M = average molecular weight of the gas

P_i = concentration of each component in the sample, vol-%

W_i = molecular weight of that component, Table A1

100 = correction for %

Table A1
Molecular Weights of Gas Sample Components

<u>Component</u>	<u>Molecular Weight</u>
Hydrogen	2.02
Nitrogen	28.01
Methane	16.04
Ethane	30.07
Ethylene	28.05
Propane	44.10
Propylene	42.08
C ₄ Paraffins	58.12
C ₄ Olefins	56.11