

TOTAL SULFUR IN LPG BY HYDROGENOLYSIS

UOP Method 923-97

SCOPE

This method is for determining total sulfur in liquefied petroleum gas (LPG) by hydrogenolysis using a commercially available analyzer. Sulfur is determined over a quantitative range of 0.1 to several hundred mass-ppm. This method cannot be used on LPG samples containing halogens at concentrations greater than ten times the sulfur level.

OUTLINE OF METHOD

The sample is subjected to hydrogenolysis, via a hydrogen-rich carrier stream passing through a pyrolysis tube maintained at 1200°C, to convert sulfur components to hydrogen sulfide (H₂S). The hydrogenolysis product is then passed to a detector where the H₂S produces a color change on lead acetate paper. The measured color change is proportional to the quantity of sulfur in the sample. In this method, gas blends are used to calibrate the instrument. Liquid hydrocarbon blends can also be used to calibrate the instrument, but a gas blend should then be used to check the calibration.

APPARATUS

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

Cylinder, for sample collection, type 304 stainless steel, high pressure, 12,400-kPa gauge (1800-psig) maximum working pressure, 500-mL capacity, Whitey, Cat. No. 304L-HDF4-500. Equip the cylinder with two stainless steel valves, Whitey, Cat. No. SS-16DKM4-F4.

LPG sampling system, Houston Atlas, Model 690-X

Regulator, hydrogen, two-stage, high purity, Matheson Gas Products, Model 3104-350

Regulator, helium, two-stage, high purity, Matheson Gas Products, Model 3104-580

Regulator, nitrogen, two-stage, high purity, Matheson Gas Products, Model 3104-580

Sulfur analyzer, Houston Atlas, Model XVI, with microcomputer

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. MATERIAL SAFETY DATA SHEETS (MSDS) 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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REAGENTS AND MATERIALS

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

Hydrogen, 99.999%, ultra-high purity, Matheson Gas Products

Helium, 99.999%, ultra-high purity, Matheson Gas Products

Methyl mercaptan in isobutane, three standards, 5, 25 and 100 mass-ppm, respectively, in cylinder with eductor tube to allow liquid sampling, stability six months according to the supplier, Scott Specialty Gases

Nitrogen, 99.999%, ultra-high purity, Matheson Gas Products

PROCEDURE

Instrument Setup

The conditions below apply to the Houston Atlas Model XVI. If another instrument is used, see that instrument's instruction manual for the appropriate setup instructions.

1. Install the sulfur analyzer and the LPG sampling unit as recommended in the manufacturer's operating manual.
2. Adjust the hydrogen pressure to 20 psig and the hydrogen flow to 250 mL/min.
3. Adjust furnace temperature to 1200°C and preheater temperature to 250°C.

Calibration

In this section and *Sample Analysis*, attach the sample, standard or reference cylinders to the instrument to ensure that liquid LPG is being sampled. For cylinders with eductor tubes, the connection is made at the top cylinder valve; for cylinders without eductor tubes, the connection is made to the bottom cylinder valve. In order to calculate the cubic spline curve used in the linearity correction algorithm the Model XVI requires four calibration points.

1. Select an appropriate sulfur standard so that it represents the highest total sulfur concentration expected during routine analysis.
2. Select the appropriate LPG valve according to sulfur concentration in the standard. Valve 1 has a 5- μ L internal loop to run samples with sulfur concentrations ranging from 0.1 to 1 mass-ppm, while valve 2 has a 0.5- μ L internal loop to run samples with total sulfur concentrations ranging between 1 and 500 mass-ppm.
3. Select the calibration parameters listed in the instrument manual.

4. Attach the LPG calibration standard to the quick-disconnect fitting mounted on the bracket located on the right side of the LPG system (refer to the instrument manual).
 - Before opening the sample cylinder valve, turn the back pressure regulator fully clockwise for maximum back pressure. Once the sample is applied adjust the regulator so that a slow amount is being vented out. The back pressure regulator is located next to the injection valves on the LPG sampling system.
5. Select the number of injections. In order to calculate and construct the cubic spline curve used in the linearity algorithm, the Model XVI requires four calibration points. This can be accomplished by using calibration standards containing different amounts of sulfur, or using a single standard and making multiple injections while holding the lead acetate paper stationary for each calibration point. The latter approach is preferable because it requires fewer standards and avoids repeated changing of LPG calibration cylinders. Examples of this approach follow:

Example 1: Where the calibration standard contains 100 $\mu\text{g/g}$ total sulfur and the desired calibration range is from 1 to 500 $\mu\text{g/g}$. Using the 0.5- μL sampling loop, build the curve by making 5, 3, 1 and 0 injections of the standard, corresponding to 500, 300, 100 and 0 $\mu\text{g/g}$ concentrations. Then, when analyzing the references and samples, make a single injection. The printed result will be the total sulfur concentration in the sample in $\mu\text{g/g}$.

Example 2: Where the calibration standard contains 100 $\mu\text{g/g}$ total sulfur and the desired concentration range is 0.1 to 100 $\mu\text{g/g}$. Using the 0.5- μL sampling loop, build the calibration curve by making 5, 3, 1 and 0 injections of the standard, and defining the responses as 100, 60, 20 and 0 $\mu\text{g/g}$. When analyzing references or samples, make five injections. The printed result will be the total sulfur concentration in the sample in $\mu\text{g/g}$.

 - If separate standards are being used, flush the injection loop before analyzing a new standard or sample to avoid contamination.
6. Open the sample cylinder valve completely and observe the liquid stream through the sight glass. When a Steady liquid stream with no bubbles is observed, start the analysis.
 - If a steady liquid stream is not obtainable, the calibration standard cylinder must be pressurized to approximately 200 psig with nitrogen.
7. Repeat the analysis of the calibration standard a sufficient number of times to obtain a range of consistent results. Three consecutive replicates that all fall within 5% of the mean are sufficient. If this cannot be obtained, check the system for leaks or other problems, correct, and run replicates until three consecutive replicates fall within the 5% guideline.
8. Manually average the counts for each standard and enter the data into the microcomputer on the analyzer to generate the calibration curve.
9. Analyze the reference sample. If the reference sample is within the allowable difference guidelines listed in *PRECISION*, the calibration is complete. Alternately, if there is sufficient data to generate a control chart, the control limits from the chart should be used, rather than the method allowable difference.
 - Use a different standard as a reference sample than you use for calibration. For example, if you are using the 100 mass-ppm standard for calibration, use the 5 or 25 mass-ppm standard as a reference to check the calibration.

Sample Analysis

LPG samples can come from a variety of sources within the refinery. Obtain a sample of LPG, in a stainless steel cylinder, for sulfur analysis using UOP Method 516.

1. Attach the LPG sample to the quick-disconnect fitting mounted on the bracket located on the right side of the LPG system (refer to the instrument manual).
 - Before opening the sample cylinder valve, turn the back pressure regulator fully clockwise for maximum back pressure. Once the sample is applied adjust the regulator so that a slow amount is being vented out. The back pressure regulator is located next to the injection valves on the LPG sampling system.
2. Flush the injection loop with the new sample between sample analyses to avoid contamination from the previous sample.
3. Select the number of injections using the same reasoning as under *Calibration*, Step 5. For example:

Example 1: Where the 100- $\mu\text{g/g}$ standard was used to set up a 1- to 500- $\mu\text{g/g}$ calibration curve, make single injections to determine the total sulfur in the sample. If the sample concentration is below 10 $\mu\text{g/g}$, make multiple injections while holding the lead acetate paper stationary, and divide the result by the number of injections. Alternately, a new calibration curve can be constructed as in Example 2.

Example 2: Where the 100- $\mu\text{g/g}$ standard was used to create a 0.1- to 100- $\mu\text{g/g}$ calibration curve, make five sample injections to determine the total sulfur concentration in the sample. If the result exceeds 100 $\mu\text{g/g}$, construct a calibration curve as in Example 1 or make fewer injections, ratioing the result to the number of injections, i.e., if two injections were made, multiply the printed result by 2.5 (5/2).
4. Open the sample cylinder valve completely and observe the liquid stream through the sight glass. When a steady liquid stream with no bubbles is observed, start the analysis.
 - If a steady liquid stream is not obtainable, the sample cylinder must be pressurized to approximately 200 psig with nitrogen.
5. Analyze the LPG sample using the parameters selected during calibration.

CALCULATIONS

All calculations are performed by the microprocessor and printed out automatically. Report the data to one significant figure below one mass-ppm, and to two significant figures at or above one mass-ppm.

PRECISION

Repeatability

Based on two tests performed by each of two analysts on each of two different days (8 tests), the within-laboratory estimated standard deviations (esd) were calculated for sulfur at specific concentrations and are listed in the Table. Two tests performed in one laboratory by different analysts on different days should not differ by more than the allowable differences in the Table at the concentrations listed (95% probability).

Table
Repeatability

Sulfur Concentration, mass-ppm	Within-Lab esd, mass-ppm	Allowable Difference, mass-ppm
9.8	0.18	0.7
69	0.6	2

Reproducibility

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

REFERENCES

Houston Atlas Model XVI instrument manual
UOP Method 516, "Sampling of Gasolines, Distillate Fuels and C₃-C₄ Fractions"

SUGGESTED SUPPLIERS

Houston Atlas, 22001 North Park Dr., Kingwood, TX 77339 (713-348-1700)
Matheson Gas Products, Inc., P.O. Box 96, Joliet, IL 60434 (815-727-4848)
Scott Specialty Gases, 6141 Easton Rd., Plumsteadville, PA 18949 (215-766-8661)
Whitey Co., 318 Bishop Rd., Highland Heights, OH 44143 (216-473-1050)