

BUREAU OF INDIAN STANDARDS

DRAFT FOR COMMENTS ONLY

*(Not to be reproduced without permission of BIS
or used as an Indian Standard)*

भारतीय मानक मसौदा

पेट्रोलियम और उसके उत्पाद — परीक्षण पद्धतियाँ भाग XXX
गैसीय हाइड्रोकार्बन और द्रवित पेट्रोलियम गैसों में कुल वाष्पशील
सल्फर का अल्ट्रावायलेट फ्लोरोसेंस डिटेक्शन के माध्यम से निर्धारण

Draft Indian Standard

**PETROLEUM AND ITS PRODUCTS — TEST METHODS
PART XXX DETERMINATION OF TOTAL VOLATILE SULPHUR IN GASEOUS
HYDROCARBONS AND LIQUEFIED PETROLEUM GASES THROUGH
ULTRAVIOLET FLUORESCENCE DETECTION**

(ICS 75.080)

Methods of Sampling and Test for Petroleum and related
Products of Natural or Synthetic Origin (excluding bitumen)
Sectional Committee, PCD 01

Last date for receipt of comment is
10 January 2024

FOREWORD

(Formal clauses will be added later)

Some process catalysts used in petroleum and chemical refining can be poisoned when trace amounts of sulphur bearing materials are contained in the feedstock's. This test method can be used to determine sulphur in process feeds, finished products and can also be used for purposes of regulatory control.

This standard is formulated based on experience of petroleum industry laboratories and considerable assistance has been derived from ASTM D6667-2021 'Standard test method for determination of total volatile sulphur in gaseous hydrocarbons and liquefied petroleum gases by ultraviolet fluorescence'.

Generally, the instrument for testing of sulphur comprises of an injection system, horizontal furnace with combustion tube and the detector. Recently, there have been test instruments with vertical furnace, which are capable to test sulphur as low as ppb ($\mu\text{g}/\text{kg}$) levels. The operation and test conditions for testing is provided by the instrument manufacturers. This standard thus provides flexibility to test Sulphur in hydrocarbons at ppb ($\mu\text{g}/\text{kg}$) levels too.

The standard covers determination of total Sulphur by two different type of instruments one with horizontal furnace or second with vertical furnace. It has been experienced that instrument with vertical furnace and auto injectors have better precision than the instrument with horizontal furnace. Users can opt for either type of instrument as per the test requirement.

In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2: 2022 'Rules for rounding off numerical values (*second revision*)'.

1 SCOPE

This test method describes the determination of total volatile sulphur in gaseous hydrocarbons and liquefied petroleum (LP) gases, applicable to the analysis of natural, processed, intermediate, and finished products. Precision has been established for sulphur concentrations ranging from 1 mg/kg to 100 mg/kg in gaseous hydrocarbons and from 1 mg/kg to 196 mg/kg in liquefied petroleum gases. It is also suitable for LP gases with halogen content below 0.35 percent (mass/mass). However, this method does not detect sulphur compounds that do not vaporize under the specified test conditions.

2 REFERENCES

The following standards contain provisions, which through reference in this text constitute the provisions of the standards. At the time of publication, the editions indicated were valid. All standards are subject to revision and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standard indicated below:

<i>IS No. / Other Standards</i>	<i>Title</i>
IS 1447 (Part 2): 2013	Methods of sampling of petroleum and its products Part 2: Liquefied petroleum gases — Method of sampling (LPG) (<i>second revision</i>)
IP 432: 2000	Liquefied petroleum gases — Calculation method for density and vapour pressure
ASTM D1070-03(2017)	Standard test methods for relative density of gaseous fuels
ASTM D1265-23	Standard practice for sampling liquefied petroleum (LP) gases, Manual Method
ASTM D2421-21	Standard practice for interconversion of analysis of C5 and lighter hydrocarbons to gas-volume, liquid-volume, or mass basis
ASTM D3700-21	Standard practice for obtaining LPG samples using a floating piston cylinder
ASTM D5287-08(2015)	Standard practice for automatic sampling of gaseous fuels
ASTM F307-13(2020)	Standard practice for sampling pressurized gas for gas analysis

3 OUTLINE OF THE METHOD

Gaseous samples are injected through a heated valve, while LPG samples use a valve connected to a heated chamber. The sample then moves into a high-temperature combustion tube, where sulphur is converted to sulphur dioxide (SO₂) in an oxygen-rich environment. Water produced during combustion is removed, and the remaining gases are exposed to ultraviolet (UV) light, which excites the SO₂ molecules (SO₂*). When these molecules return to a stable state, they emit light that a detector measures to determine the sulphur content in the sample.

NOTE — Excessive exposure to ultraviolet light is injurious to health. The operator shall prevent exposing their person, especially their eyes, not only to direct UV light but also to secondary or scattered radiation that is present.

4 SIGNIFICANCE AND USE

The sulphur content in liquefied petroleum gas (LPG), which is utilized as a fuel, contributes to the formation of sulphur oxides (SO_x) emissions and can lead to corrosion in engine and exhaust systems. Additionally, certain process catalysts used in petroleum and chemical refining can be adversely affected by sulphur-containing materials present in the feedstocks. This test method is applicable for determining sulphur levels in process feeds, assessing sulphur in finished products, and can also be employed for compliance verification when accepted by regulatory authorities.

5 APPARATUS

5.1 Furnace

Utilize an electric furnace maintained at a temperature of (1075 ± 25) °C, which is sufficient to completely pyrolyze the sample and converts sulphur to sulphur dioxide (SO₂).

5.2 Combustion Tube

Employ a quartz combustion tube designed for the direct injection of the sample into the heated oxidation zone of the furnace. The combustion tube shall have side arms for the introduction of both oxygen and carrier gas. The oxidation section shall be adequately sized to ensure complete combustion of the sample (*see 11.3*). Fig. 1 represents a typical combustion tube.

5.3 Flow Control

The apparatus shall be equipped with flow controllers that can maintain a consistent supply of oxygen and carrier gas at the specified flow rates.

5.4 Drier Tube

Incorporate a mechanism for removing water vapour generated during the combustion of the sample. This can be achieved using a membrane drying tube or a permeation dryer that utilizes selective capillary action for effective water removal.

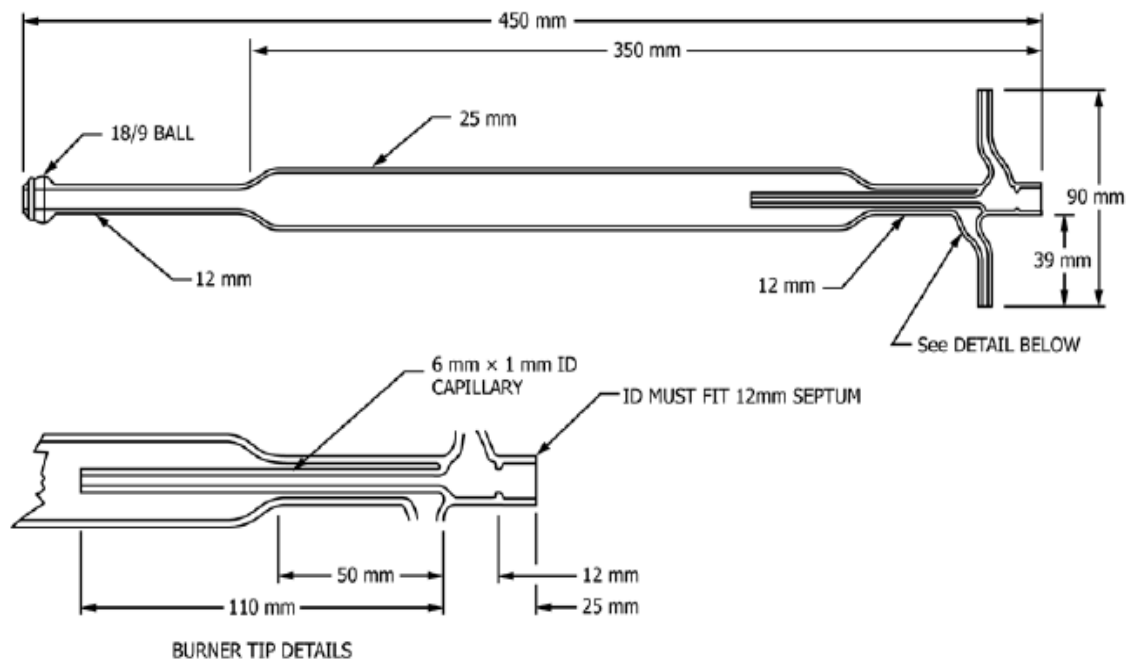


FIG. 1 EXAMPLE OF A TYPICAL DIRECT INJECT QUARTZ PYROLYSIS TUBE

5.5 UV Fluorescence Detector

Use a quantitative detector capable of measuring the light emitted from the fluorescence of sulphur dioxide when exposed to ultraviolet (UV) light.

5.6 Sample Inlet System

The system provides a heated gas-sampling valve, or a LP gas-sampling valve, or both, with a heated expansion chamber, connected to the inlet of the oxidation area, Fig. 2.

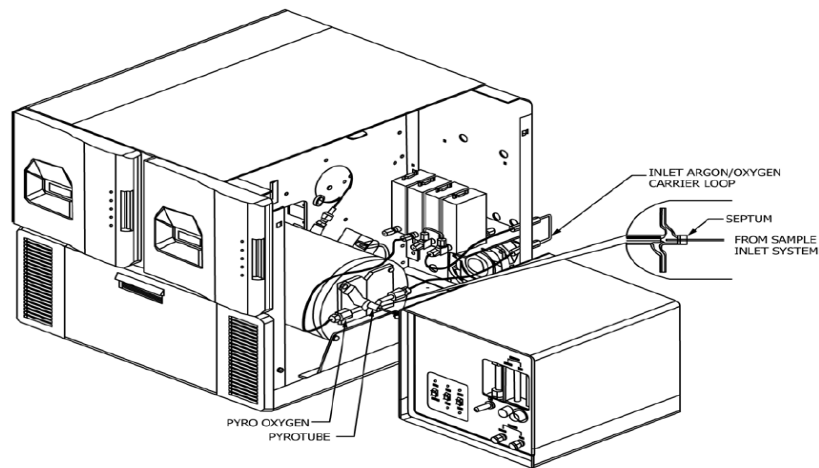


FIG. 2 EXAMPLE OF ORIENTATION OF TOTAL SULPHUR ANALYSER AND GAS OR LIQUID SAMPLING VALVE

The system is purged/flushed by an inert carrier gas and shall be capable of allowing the quantitative delivery of the material to be analysed into the oxidation zone at a controlled and repeatable rate of approximately 30 ml/min. Fig. 3 displays an example.

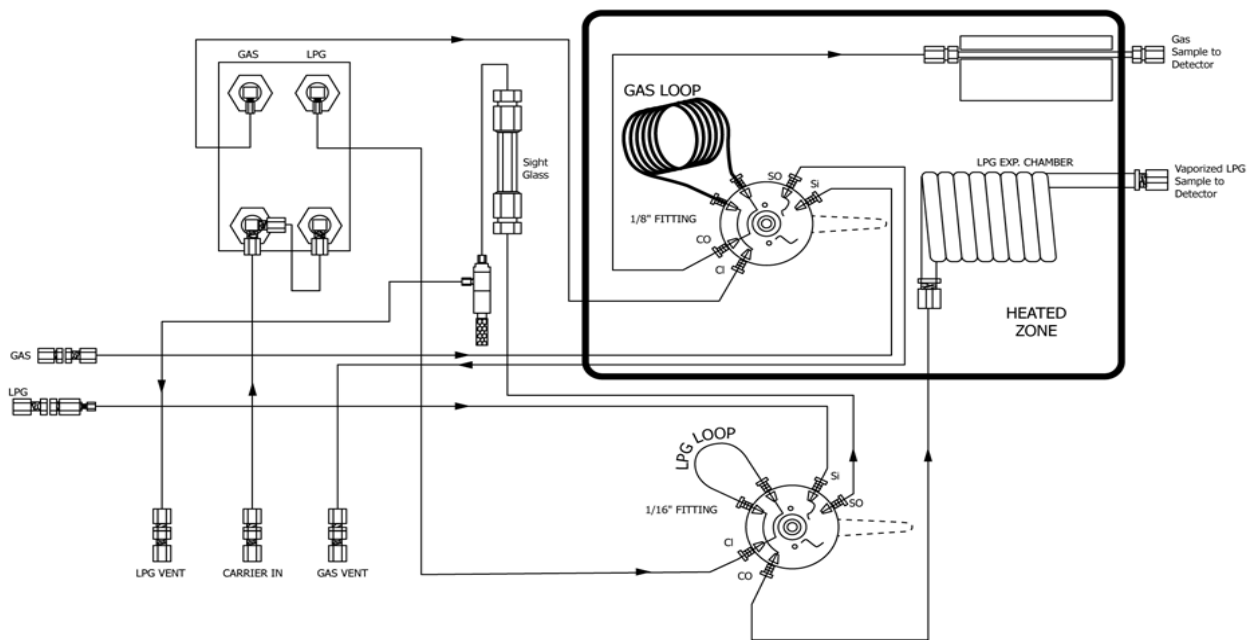


FIG. 3 SAMPLE INLET SYSTEM FLOW PATH

5.7 Electronic system to record measurement data, strip chart recorder, equivalent electronic data logger, integrator or, recorder (optional).

6 REAGENTS

6.1 Follow Safety Data Sheet (SDS) of reagents for safety precautions/considerations.

NOTES

1. Requirement of reagents and chemicals may slightly differ for instruments from different manufacturers. However, for such selection, recommendation of the instrument manufacturer shall be followed.
2. High temperature is employed in this test method. Since the instrument is operated at high temperature, exercise care when using flammable materials near the pyrolysis furnace.

6.2 Quality of Reagents

Unless stated otherwise, only 'Analytical Grade' chemicals shall be utilized for testing. It is essential to verify that the reagent possesses a high enough purity to ensure that its use does not compromise the accuracy of the analysis.

NOTE — 'Pure chemicals' shall mean chemicals that do not contain impurities which affect the validity of results of analysis.

6.3 Magnesium Perchlorate Mg (ClO₄)₂

For drying products of combustion (permeation drier is not used).

6.4 Inert Gas

Use high-purity inert gases, such as argon or helium, with a minimum purity of 99.998 percent. The moisture content should not exceed 5 mg/kg.

NOTE — Argon or helium are usually available as compressed gas under high pressure.

6.5 Oxygen

Minimum purity of 99.75 percent, classified as high purity, with a maximum moisture content of 5 mg/kg, and dried accordingly

6.6 Calibration Standards

Certified Calibration Standards or Certified Reference Materials (CRMs) obtained from commercial sources, as well as calibration gases produced using certified permeation tube devices, are necessary. Table 1 details the sulphur source materials and diluent matrices utilized in the inter-laboratory study.

Table 1
(Clause 6.6)

SI No. (1)	Sulphur Compound (2)	Diluent matrix (3)
i)	Dimethyl sulphide	<i>n</i> - butane
		iso-butane
		Propylene
		Propane

NOTE

- 1 Other sulphur sources and diluent materials may be used if precision and accuracy are ensured and maintained.
- 2 Calibration standards are typically re-mixed and re-certified on a regular basis depending upon frequency of use and age. These calibration standards usually have a useful shelf life of about 6 months to 12 months.

6.7 Quality Control (QC) Samples

Quality Control Samples shall be prepared from portions of one or more gas or LP gas materials that are stable and representative of the samples of interest.

7 SAMPLING

7.1 Collect a representative sample in accordance with Practices IS 1448 Part 2, ASTM F307, ASTM D1265, D3700, D5287 as applicable. Samples to be analysed as soon as possible after taking from bulk supplies to prevent loss of sulphur or contamination due to exposure or contact with sample containers.

7.2 If the sample is not used immediately, then thoroughly mix it in its container prior to taking a test sample. The use of segregated or specially treated sample containers can help reduce sample cross-contamination and improve sample stability.

8 APPARATUS ASSEMBLY

8.1 Assemble and check the apparatus for leaks as per manufacturer's instructions.

8.2 Typical apparatus adjustments and conditions are listed in Table 2 below.

Table 2 Typical Operating Conditions
(Clauses 8.2 and 10.3)

SI No.	Components	Conditions
(1)	(2)	(3)
i)	Sample inlet system temperature	(85 ± 20) °C
ii)	Sample injection system carrier gas	25 ml/min to 30 ml/min
iii)	Furnace temperature	(1075 ± 25) °C
iv)	Furnace oxygen flow meter setting	375 ml/min to 450 ml/min
v)	Inlet oxygen flow meter setting	10 ml/min to 30 ml/min
vi)	Inlet carrier flow meter setting	130 ml/min to 160 ml/min
vii)	Gas sample size	10 ml to 20 ml
viii)	LPG sample size	Typically, 15 µl

Adjust instrument sensitivity and baseline stability and perform instrument-blanking procedures as prescribed in equipment manual.

9 HAZARDS

High temperature, flammable hydrocarbons, and gases under high pressures occur in the test method. Use materials that are rated for containing these pressurized hydrocarbons in all sample containers and sample transfer apparatus. Exercise extra care when using flammable materials near the oxidative furnace.

10 CALIBRATION AND STANDARDISATION

10.1 Refer to Table 3 to select an appropriate calibration range based on the expected sulphur concentrations in the samples to be analyzed. It is preferable to use a sulphur compound along with a diluent.

Table 3 Typical Sulphur Calibration Ranges and Standard Concentrations
(Clauses 10.1 and 10.3)

SI No. (1)	Curve I Sulphur (mg/kg) (2)	Curve II Sulphur (mg/kg) (3)	Curve III Sulphur (mg/kg) (4)
i)	Blank	Blank	Blank
ii)	5	10	50
iii)	10	50	100
iv)	-	100	200

NOTE — The number of standards used per curve varies depending upon the analytical requirement.

10.2 With the sample valve in the ready to inject position, connect the pressurized sample container to the sample valve of the sample inlet system.

10.3 A quantitative measurement of the injected material can be obtained by filling the sample loop of the sample valve system for the matrix being analysed (refer Table 2 and Notes below).

NOTES

- 1 Injection of a constant or similar sample size for all materials analysed in a selected operating range promotes reliable combustion conditions and may simplify result calculations.
- 2 An automatic sample transfer and injection device i.e. auto sampler/ auto sampler cum injector may be used.

10.3.1 Flush the sample loop with sufficient calibration material to assure that the material to be injected is representative.

10.3.2 For samples of liquefied petroleum gas (LPG), if bubbles are visible in the liquid column, flush the sample loop to introduce a new liquid-filled sample portion.

10.4 Start the analyser and inject the calibration material according to the manufacturer's instructions.

10.5 Calibration of the instrument can be performed using one of the following methods:

10.5.1 *Multi-point Calibration*

10.5.1.1 If the apparatus includes an internal self-calibration feature, analyze the calibration standards and blank three times using the procedures outlined in (*see 10.2 to 10.4*).

10.5.1.2 Calibrate the analyzer according to the manufacturer's instructions to determine sulphur concentration (*see 14*). This calibration curve is generally linear, and system performance should be verified at least once daily during use.

NOTE — Other calibration curve techniques can be used when accuracy and precision are ensured. The frequency of calibration may be determined by the use of quality control charts or other quality assurance/quality control techniques.

10.5.2 *One-point Calibration*

10.5.2.1 Use a calibration standard (*see 6.6*) with a sulphur content that is close to that of the samples being analyzed (within ± 25 percent maximum).

10.5.2.2 Follow the manufacturer's instructions to establish an instrument zero (blank) by conducting an analysis run without injecting the calibration standard.

10.5.2.3 Measure the calibration standard at least three times.

10.5.2.4 Calculate a calibration factor (K) in counts per nanogram of sulphur (counts/ng S) (*see 12.2*).

11 PROCEDURE

11.1 Obtain a test specimen by following the procedure outlined in (*see 7*). Typically, the sulphur concentration in the test specimen should be lower than that of the highest standard and higher than that of the lowest standard used in the calibration.

11.2 Measure the response of the test specimen using one of the methods (*see 10.2 to 10.4*).

11.3 Inspect the combustion tube and other flow path components to ensure complete oxidation of the test specimen.

11.3.1 If coke or sooting is observed, then reduce the rate of injection or the sample size, or both, of the sample into the furnace.

11.4 Cleaning and Re-calibration

Clean any components that have become coked or sooted according to the manufacturer's instructions. After cleaning or making adjustments, reassemble and check the apparatus for leaks. Repeat the instrument calibration before reanalyzing the test specimen.

11.5 To obtain a single result, measure each test specimen three times and calculate the average detector response.

11.6 Density values required for calculations should be measured according to (*see 12.2.3*), at the temperature at which the sample is tested.

NOTE — When sample matrix compositions are known, other techniques may be used to derive sample density, provided accuracy and precision are ensured.

12 CALCULATION

12.1 This section explains the calculation procedure for different calibration options and for correction of the Sulphur result when the sample is different from the composition of the calibration material.

When the sample is injected in the liquid phase, the density of the calibration mixture and the sample are essential to calculate the results **12.2 to 12.4**.

When the sample is injected in the gas phase, the molecular weight of the calibration mixture and the samples are essential to calculate the results **12.5** to **12.7**.

12.2 To calculate the density of the liquid calibration mixture and/or the sample:

12.2.1 *Interconversion to Liquid Volume percent from Mass percent According to Practice ASTM D2421*

$$\text{Liquid Volume percent } x = 100 \times \frac{(\text{Mass percent}_x / \text{Relative Density}_x)}{\sum_{N=1}^{\#comp} (\text{Mass percent}_n / \text{Relative Density}_n)}$$

where

Liquid Volume percent = liquid volume percent of all identified components in the sample of which x is one;

#comp = the number of identified components in the sample of which x is one;

Relative Density x = the value (taken from Practice ASTM D2421, Table 2, Column 3) given for each identified component x as a liquid;

Mass percent x = the weight percent of each identified component taken from GC analysis such as D2163; and

$\sum_{N=1}^{\#comp}$ = the sum of the quotients Mass percent divided by the relative density for all identified components.

12.2.2 *Interconversion to Liquid Volume percent from Mole percent according to practice ASTM D2421*

$$\text{Liquid Volume } x = 100 \times \frac{(\text{Mole percent } x \times \text{Volume Ratio } x)}{\sum_{N=1}^{\#comp} (\text{Mole percent } n \times \text{Volume Ratio } n)}$$

where

Liquid Volume percent x = liquid volume percent of all identified components in the sample of which x is one;

#comp = the number of identified components in the sample of which x is one;

Volume Ratio x = the value (taken from Practice ASTM D2421, Table 2, Column 2) given for each identified component x ;

Mole percent x = the mole percent of each identified component taken from GC analysis (equivalent to gas volume percent assuming an ideal gas); and

$\sum_{n=1}^{\#comp}$ = the sum of the quotients Mole percent n multiplied by the volume ration for all identified components.

12.2.3 *Relative Density Calculation According to Practice D2598*

$$\text{Relative Density}_{\text{mix}} = \sum_{x=1}^{\#comp} \left(\frac{\text{Liquid Volume percent}_x \times \text{Relative Density}_x}{100} \right) \dots\dots (3)$$

where

Relative Density mix = relative density of the LPG mixture,

#comp = the number of identified components in the sample of which x is one;

Relative Density x = liquid relative density of each component of which x is one;

Liquid Volume percent x = liquid volume percent of all identified components in the sample of which x is one; and

$\sum_{n=1}^{\#comp}$ = the sum of the relative density of each component of which x is one.

12.3 For analysers calibrated using an internal self-calibration and when the liquid phase sample is injected, calculate the sulphur content in the test sample as follows:

$$\text{Sulphur, mg/kg} = \frac{G \times d}{s}$$

where

d = density of standard mixture, g/ml;

s = density of sample, g/ml; and

G = sulphur observed in test sample, mg/kg.

12.4 For analysers calibrated using a one-point calibration and when the liquid phase sample is injected, calculate the calibration factor, **(10.5.2.4)**,

$$K = \frac{Ac}{Mc \times Scg}$$

Or

$$K = \frac{Ac}{Vc \times Scv}$$

where

Ac = integrated detector response for calibration standard, in counts, and

Mc = mass of calibration standard injected, in milligrams, either measured directly or calculated from measured volume injected and density.

$$Mc = V \times Dc$$

where

Dc = density of calibration standard at measurement temperature, g/ml;

Vc = volume of calibration standard injected, μ l;

Scg = sulphur content of calibration standard, ml/kg; and

Scv = sulphur content of calibration standard, mg/l.

12.4.1 Calculate the average of the calibration factor (K) and check that the standard deviation is within the accepted tolerance limit. This calibration factor shall be proven every day.

12.4.2 Calculate the sulphur content, S , of the sample, in mg/kg, using the following equation

$$S = \frac{A}{M \times K \times Fg}$$

Or

$$S = \frac{A}{V \times K \times Fv}$$

where

K = calibration factor, in counts per nanogram of sulphur; and

M = mass of test sample solution injected, in milligrams, either measured directly or calculated from measured volume injected and density.

$$M = V \times D$$

where

D = density of test sample solution at measurement temperature, g/ml;

V = volume of the injected test sample solution, μl ;

A = integrated detector response for sample, in counts number;

Fg = gravimetric dilution factor, mass of test sample/ mass of test sample and solvent, g/g; and

Fv = volumetric dilution factor, mass of test sample/volume of test sample and solvent, g/ml.

12.5 To calculate the molecular weight of the gas calibration mixture or sample, or both:

12.5.1 Inter-conversion to mole (gas vol) percent from mass percent according to Practice ASTM D2421:

$$\text{Mol percent } x = 100 \times \frac{(\text{Mass percent } x / \text{Molecular Mass } x)}{\sum_{N=1}^{\#comp} (\text{Mass percent } n / \text{Molecular Mass } n)}$$

where

Mole percent x = mole percent of all identified components in the sample of which x is one;

#comp = the number of identified components in the sample of which x is one;

Molecular Mass = the value (taken from Practice ASTM D2421, Table 2, Column 1) given for each identified component x ;

Mass percent x = the weight percent of each identified component taken from GC analysis; and

$\sum_{n=1}^{\#comp}$ = the sum of the quotients mass percent divided by the molecular mass for all identified components.

12.5.2 Calculation of the mole mass of the mixture:

$$\text{Molecular Weight}_{\text{mixture}} (\text{g/mol}) = \frac{x_1 \times M_1 + x_2 \times M_2 + \dots x_n \times M_n}{100}$$

where

x = mole percent of all components; and

M = the molecular mass of each gas.

12.6 For analysers calibrated using an internal self-calibration and when the sample in gas phase is injected, calculate the sulphur content in the test sample as follows:

$$\text{Sulphur (mg/kg)} = \frac{G \times \text{Molecular Mass}_x}{\text{Molecular Mass}_y}$$

where

Molecular Mass x = molecular weight of standard mixture, g/mol;

Molecular Mass y = molecular weight of sample, g/mol; and

G = Sulphur found in test sample, mg/kg.

12.7 For analysers calibrated using a one-point calibration and when the sample in gas phase is injected, calculate the calibration factor, (10.5.2.4).

$$K = Ac / mc \times Scg$$

Or

$$K = Ac / Vc \times Scv$$

where

A_c = integrated detector response for calibration, in counts, and

m_c = mass of calibration standard injected, in milligrams, either measured directly or calculated from measured volume injected and molecular mass.

$$m_c = V \times \text{Molecular Mass } x$$

where

Molecular Mass x = molecular weight of calibration standard; g/mol,

V_c = volume of calibration standard injected, μl ;

S_{cg} = Sulphur content of calibration standard, ml/kg; and

S_{cv} = Sulphur content of calibration standard, mg/l.

12.7.1 Calculate the average of the calibration factor (K) and check that the standard deviation is within the tolerance accepted. This calibration factor shall be established every day or day of use.

12.7.2 Calculate the Sulphur content, S , of the sample in mg/kg, using the following equation:

$$S = A/m \times K \times F_g$$

Or

$$S = A/V \times K \times F_V$$

where

K = calibration factor, in counts per nanogram of Sulphur; and

m = mass of test sample solution injected, in milligrams, either measured directly or calculated from measured volume injected and molecular mass.

$$m = V \times \text{Molecular Mass } y$$

where

Molecular Mass y = molecular weight of test sample solution, g/mol;

V = volume of the test sample solution injected, μl ;

A = integrated detector response for sample, in counts number;

F_g = gravimetric dilution factor, mass of test sample/mass of test sample and solvent, g/g, and;

F_V = volumetric dilution factor, mass of test sample/volume of test sample and solvent, g/ml.

13 REPORT

13.1 For sulphur results that are equal to or exceed 10 mg/kg, report the values rounded to the nearest mg/kg. For results below 10 mg/kg, report the values rounded to the nearest 0.1 mg/kg.

14 QUALITY CONTROL

14.1 Confirm the performance of the instrument or the test procedure by analysing a Quality Control (QC) sample (*see 6.7*) after each calibration and at least each day of use thereafter (*see 11.5*).

14.1.1 When QC/Quality Assurance (QA) protocols are already established in the testing facility, these may be used when they confirm the reliability of the test result.

14.1.2 When there is no QC/QA protocol established in the testing facility, Annex A may be used as the QC/QA system.

15 PRECISION AND BIAS

15.1 The following precision and bias data was derived from two separate interlaboratory studies.

15.2 Repeatability

The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values in only 1 case in 20, where X = the average of the two test results. For gaseous hydrocarbons with sulphur in the range of 1 mg/kg to 100 mg/kg:

$$r = 0.1152 (X)$$

For LP gases with sulphur in the range of 1 mg/kg to 196 mg/kg:

$$r = 0.2707 (X)^{0.7}$$

15.3 Reproducibility

The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values in only 1 case in 20, where X = the average of the two test results. For gaseous hydrocarbons with sulphur in the range of 1 mg/kg to 100 mg/kg:

$$R = 0.3130 (X)$$

For LP gases with Sulphur in the range of 1 mg/kg to 196 mg/kg:

$$R = 2.3205 (X)^{0.7}$$

15.4 Bias

Bias for this test method was studied during the inter-laboratory study by analysis of certified-gravimetrically prepared calibration standards and sample materials and published in 2000 as a research report. This report indicated that the results obtained were within the repeatability of the test method.

15.5 Examples of the above precision estimates for selected absolute values of X are set out in Table 4.

Table 4 Repeatability (r) and Reproducibility (R)
(Clause 15.5)

Sl No.	Concentration	Repeatability		Reproducibility	
	S (mg/kg)	Gaseous Hydrocarbons	LPG	Gaseous Hydrocarbons	LPG
(1)	(2)	(3)	(4)	(5)	(6)
i)	1	0.1	0.3	0.3	2.3
ii)	5	0.6	0.8	1.6	7.2
iii)	25	2.9	2.6	7.8	22
iv)	50	5.8	4.2	16	36
v)	100	12	6.8	31	58
vi)	150	N/A	9	N/A	77
vii)	196	N/A	11	N/A	93

N/A—Not applicable to the scope of Gaseous Hydrocarbons.

ANNEX A
(Clause 14.1.2)

A-1 QUALITY CONTROL MONITORING

A-1.1 Confirm the effectiveness of the instrument or testing procedure by analyzing quality control (QC) samples.

A-1.2 Before monitoring the measurement process, determine the average value and control limits for the QC sample.

A-1.3 Record the results of the QC analysis and evaluate them using control charts or other statistically valid methods to assess the overall control status of the testing process. Investigate any data that falls outside of control limits to identify potential causes. This investigation may lead to recalibrating the instrument.

NOTE — A-1.1—In the absence of explicit requirements given in the test method, A-1.4 provides guidance on QC testing frequency.

A-1.4 In the absence of specific requirements in the test method, the frequency of QC testing should be based on the critical nature of the quality being measured, the stability of the testing process, and customer demands. Generally, a QC sample should be tested each day samples are analyzed. If a large volume of samples is processed, increase the QC testing frequency. However, if the testing process is shown to be statistically stable, the frequency may be reduced.

A-1.5 Regularly compare the precision of QC sample testing against the established precision to ensure the quality of the data.

A-2 OPERATION SUGGESTIONS AND SAFETY ASPECTS

A-2.1 Prior to sample injection, ensure that the apparatus is fully stabilized and ready for analysis according to the manufacturer's instructions.

A-2.2 Keep the valves in the sample inlet system in the load position except during the actual sample analysis.

A-2.3 After filling the sample valve and allowing it to equilibrate, execute a quick and complete rotation of the sample valve to switch to the inject position for sample injection.

A-2.4 Keep the sampling valve in the inject position until the analysis is complete, which is indicated by the instrument returning to baseline and finishing the integration process.

A-2.5 The time required for the detector to respond can vary based on the type of pyrotube used, the carrier gas, and the sample size or sulphur concentration. Typical response times can range from 20 s to 1 min (refer Fig. A-2.1).

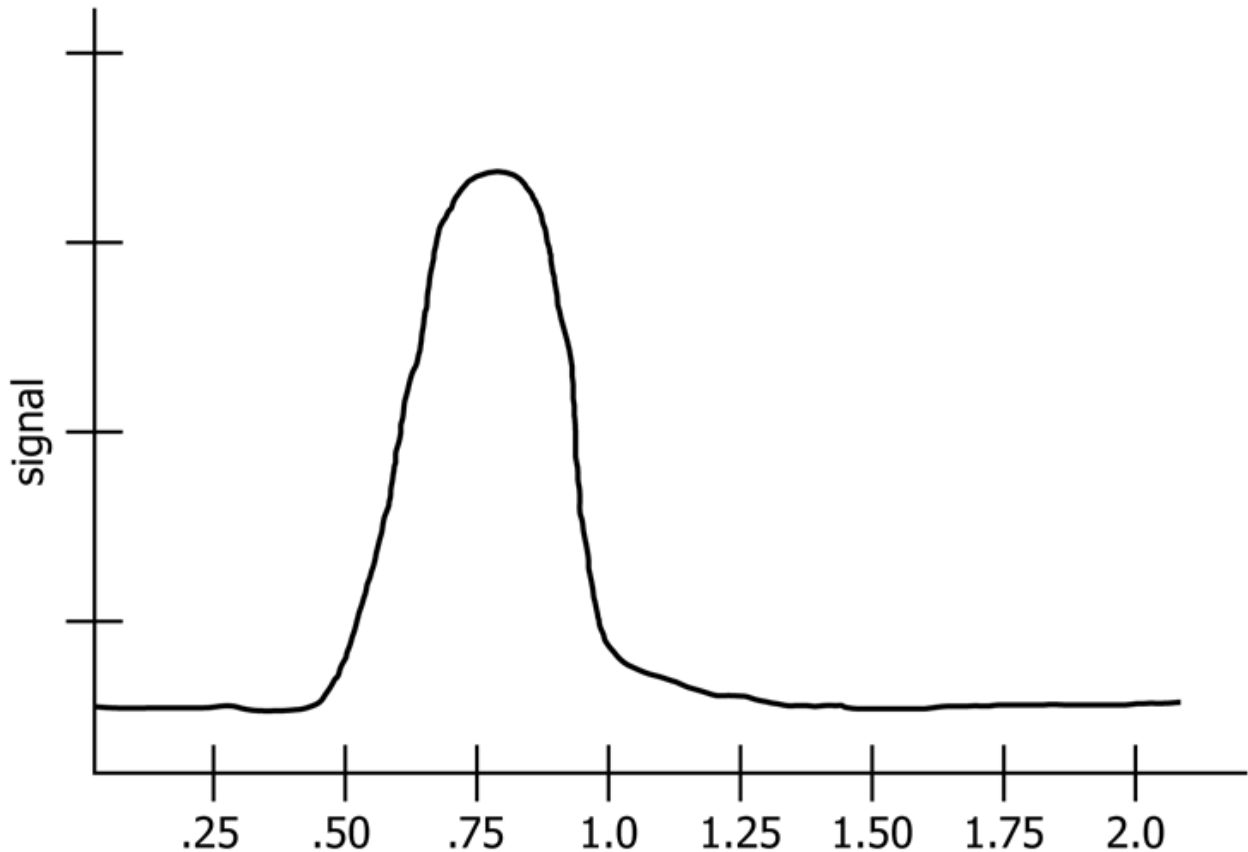


FIG. A-2.1 TYPICAL INJECTION PROFILE

A-2.6 Adjust the carrier gas flow rates in the sample inlet system to optimize sample combustion and detection characteristics. However, avoid excessive flow rates (over 30 ml/min) as they may lead to incomplete combustion and sooting.

A-2.7 Allow sufficient time for the signal to return to baseline between successive injections to ensure accurate measurements.

A-2.8 For sample cylinders containing liquefied petroleum gases, maintain adequate pressure (generally above 200 psig) to facilitate sample transfer without bubble formation in the transfer tubing and sight glass.

A-2.9 Utilize standard gas flow conditions that are appropriate for your analyzer to ensure consistent and reliable results. (*see 9*) of the test method

A-2.10 It is highly recommended to incorporate a filtering device before introducing the sample. This practice can significantly prolong the lifespan of the valves and prevent blockages in the transfer tubing.

A-2.11 Opt for low or iron-free alloys and/or inert-treated materials to enhance the accuracy of analyses, particularly for low-level sulphur concentrations.

A-2.12 The use of a strip-chart recorder or a software peak display can aid in the set up and normal operation of the sample inlet system.

A-2.13 Quality analytical results are best obtained when calibration materials match the matrix of the samples analysed. Injection of solvent (room temperature) liquids as calibrants or samples is discouraged and can cause severe coking (sooting) of sample flow path components and yield poor analytical results.

A-3 SAFETY ASPECTS

A-3.1 Regularly check the transfer lines and fittings that connect the sample container to the sample inlet system for any leaks or signs of stress weakening, which may occur due to frequent bending, aging, or usage.

A-3.2 Routinely inspect quick-connect fittings and other components used for sample transfer and venting to ensure they are leak-free and functioning properly.

A-3.3 Ensure that waste gases from the sample inlet system are vented to an area that is away from the instrument's operating environment and any potential ignition sources.

A-3.4 Maintain the pressure in sampling cylinders and during sample transfer at levels typically below 750 psig. Do not exceed the overall pressure rating (900 psig) of the sample inlet system or the capacity of the sample transfer equipment being used.

A-3.5 Apply slow to moderate purge rates when filling the sample loops during the sample-loading phase of the sampling procedure.

A-3.6 After loading the sample loop, allow the pressure within the loop and vent system to equilibrate. Utilizing a secure gas-bubble monitoring device that vents to a safe area can provide visual confirmation and help ensure consistent sample sizes during injection.

A-3.7 After completing the sampling process, it is advisable to perform a controlled venting or relief of pressure from the sample transfer line.

A-3.8 After analysis, with the sample valves set to the load position, connect an inert gas to the sample inlet system to purge any remaining sample residue.

A-4 CALCULATION EXAMPLES FOR CORRECTION OF THE SULPHUR RESULT BASED ON THE MATRIX COMPOSITION

A-4.1 Calculation example for the correction for samples injected in the liquid phase according to **12.2** to **12.4**.

A-4.1.1 *Step 1—Interconversion to Liquid Volume percent*

A sample calculation using the hypothetical LPG compositional analysis is given in Table A-4.1.

A-4.1.2 *Step 2—Relative Density Calculation of the Mixture:*

$$\text{Relative Density} = \sum_{n=1}^{\#comp} \times \left(\frac{\text{Liquid Volume}\%_x \times \text{Relative Density}_x}{100} \right) =$$
$$\frac{(0.07 \times 0.35639) + (80.57 \times 0.50736) + (5.09 \times 0.56293) + (14.27 \times 0.58407)}{100}$$

A-4.1.3 *Step 3—Correct for Density Difference between the LPG Sample and Calibration Material*

The example test result provides a sulphur content of 50 mg/kg, the calibration gas used is a sulphur standard in butane with a relative density of 0.5842.

$$\text{Corrected result} = 0.5842/0.5210 \times 50 = 56 \text{ mg/kg (A-4.2)}$$

A-4.2 Calculation example for the correction for samples injected in the gas phase according to **12.5** to **12.7**.

Table A-4.1 Conversion from Mass percent to Liquid Volume percent for Selected Properties
(Clause A-4.1.1)

SI No.	LPG	Mass percent	Mass percent Relative Density (kg/m ³) a	Quotient Mass percent / Relative Density	Liquid Volume percent (V/V percent) Multiply by Normalization Factor
(1)	(2)	(3)	(4)	(5)	(6)
i)	Methane	0	0.3	0	0
ii)	Ethane	0.05	0.35639	0.14	0.07
iii)	Propane	78.45	0.50736	154.624	80.57
iv)	Isobutane	5.5	0.56293	9.77	5.09
v)	<i>n</i> -butane	16	0.58407	27.394	14.27
vi)	Total	100		191.928	100

A-4.2.1 Step 1 — Interconversion to Mole percent

A sample calculation using the hypothetical LPG compositional analysis is given in Table A-4.2 column 1 and 2. The results of the conversion from mass percent to mole is shown in Table A-4.2 column 3 to 5.

A-4.2.2 Step 2—Molecular Weight Calculation of the Mixture According:

$$\text{Molecular Weight mixture (g/mol)} = \frac{x_1 \times M_1 + x_2 \times M_2 + \dots + x_n \times M_n}{100} = \frac{0.08 \times 30.07 + 82.72 \times 44.10 + 4.40 \times 58.12 + 12.80 \times 58.12}{100}$$

$$= 46.50$$

A-4.2.3 Step 3 — Correct for Molecular Weight Difference between the LPG and the Calibration Material

The example test result provides a sulphur content of 50 mg/kg, the used calibration gas is a sulphur standard in butane with a molecular weight of 58.12 g/mol.

$$\text{Corrected result} = 58.12/46.5 \times 50 = 62 \text{ mg/kg (A-4.4)}$$

Table A-4.2 Conversion of Mass percent to Mole percent for Selected Properties
(Clause A-4.2.1)

Sl. No.	LPG Components	Mass percent	Mass percent Relative Density (kg/m ³) A	Quotient Mass percent / Relative Density	Liquid Volume percent (V/V percent) Multiply by Normalization Factor
(1)	(2)	(3)	(4)	(5)	(6)
i)	Methane	0	16.04	0	0
ii)	Ethane	0.05	30.07	0.0017	0.08
iii)	Propane	78.45	44.1	1.7791	82.72
iv)	Isobutane	5.5	58.12	0.0946	4.4
v)	<i>n</i> -butane	16	58.12	0.2753	12.8
vi)	Total	100		2.1507	100

NOTE— Normalization factor is calculated by 100 divided by the sum of all the individual quotients in col (4).