Doc. No: PCD 1 (23728)P
October 2023

BUREAU OF INDIAN STANDARDS
DRAFT FOR COMMENTS ONLY
(Not to be reproduced without permission of BIS or used as an Indian Standard)

Draft Indian Standards

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

(ICS No. 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 9 November 2023

FOREWORD

(*Formal clause 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 feedstocks. 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 (µg/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 (µg/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

1.1 This standard prescribes method of test for determination of total volatile sulphur in gaseous hydrocarbons and liquefied petroleum (LP) gases. This test method can be applied to analyse natural, processed, intermediates and finished products.

1.2 Precision has been determined for sulphur in gaseous hydrocarbons in the range of 1 mg/kg to 100 mg/kg and for sulphur in liquefied petroleum (LP) gases in the range of 1 mg/kg to 196 mg/kg.
1.3 This test method also applies to determine total volatile Sulphur in LP gases containing less than 0.35 percent (mass/mass) halogen(s).

1.4 This test method does not detect sulphur compounds that do not vaporize under the conditions of the test.

1.5 This standard may involve hazardous materials, operations and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limits prior to use.

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:

IS / International Standard No.	*Title*
IS 1447 [Part 2] : 2013	Methods of sampling of petroleum and its products Part 2: Liquefied petroleum gases - Method of sampling (LPG) (*second revision*)
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 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
Gas Processor Association (GPA) Standards:5 GPA 2166-17	Obtaining natural gas samples for analysis by gas chromatography
Gas Processor Association (GPA) Standards:5 GPA 2174-14	Obtaining liquid hydrocarbon samples for analysis by gas chromatography

3 OUTLINE OF THE METHOD

Gaseous samples are injected through a heated sample valve. Liquefied petroleum gas (LPG) samples are injected by a sample valve connected to a heated expansion chamber. The gaseous sample then enters a high temperature combustion tube where sulphur is converted to sulphur dioxide (SO_2) in an oxygen rich atmosphere. Water produced during the sample combustion as a result of combustion is removed and the sample combustion gases are exposed to ultraviolet (UV) light. The SO_2 absorbs the energy from the UV light to convert to an excited sulphur dioxide (SO_2). Fluorescence emitted from the excited state SO_2* on its return to a stable ground state SO_2* is detected by a photomultiplier tube, the resulting signal is a measure of 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 of LPG, used for fuel purposes, contributes to SOx emissions and can lead to corrosion in engine and exhaust systems. Some process catalysts used in petroleum and chemical refining can be poisoned by sulphur bearing materials in the feed stocks. This test method can be used to determine sulphur in process feeds, to measure sulphur in finished products, and can also be used for compliance determinations when acceptable to a regulatory authority.

5 APPARATUS

5.1 Furnace — An electrically heated furnace maintained at a temperature (1075 °C ± 25 °C) sufficient to pyrolyze/ combust the entire sample and converts sulphur to SO_2 (Sulphur di oxide).

5.2 Combustion Tube — A quartz combustion tube constructed to allow the direct injection of the sample into the heated oxidation zone of the furnace. The combustion tube to have provisions of side arms for the introduction of oxygen and carrier gas. The oxidation section shall be large enough (Fig. 1) to ensure complete combustion of the sample (11.3). Fig. 1 represents a typical combustion tube. Other configurations are acceptable when precision of test method is ensured and maintained.

5.3 Flow Control — The apparatus shall be furnished with flow controllers capable of maintaining a constant supply of oxygen and carrier gas at the identified rates.

5.4 Drier Tube — The apparatus shall be furnished with a mechanism for the removal of water vapour formed during sample combustion. This can be achieved with a membrane drying tube, or a permeation dryer that uses a selective capillary action for water removal.

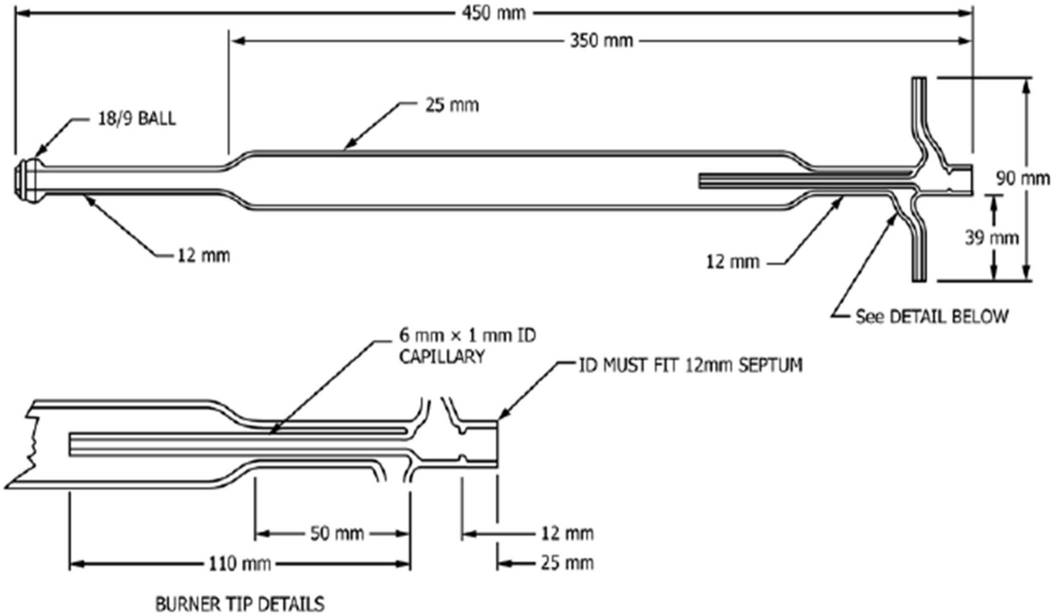

FIG. 1 EXAMPLE OF A TYPICAL DIRECT INJECT QUARTZ PYROLYSIS TUBE

5.5 UV Fluorescence Detector — A quantitative detector capable of measuring light emitted from the fluorescence of sulphur dioxide by 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.

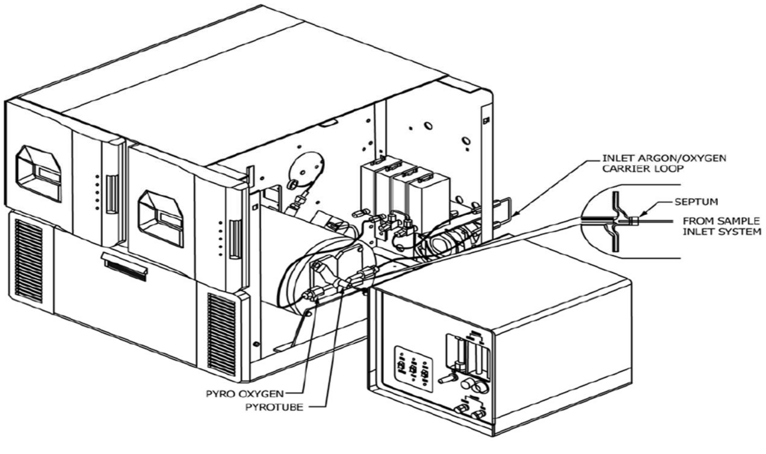

FIG. 2 EXAMPLE OF ORIENTATION OF TOTAL SULPHUR ANALYSER AND GAS OR LIQUID SAMPLING VALVE

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.

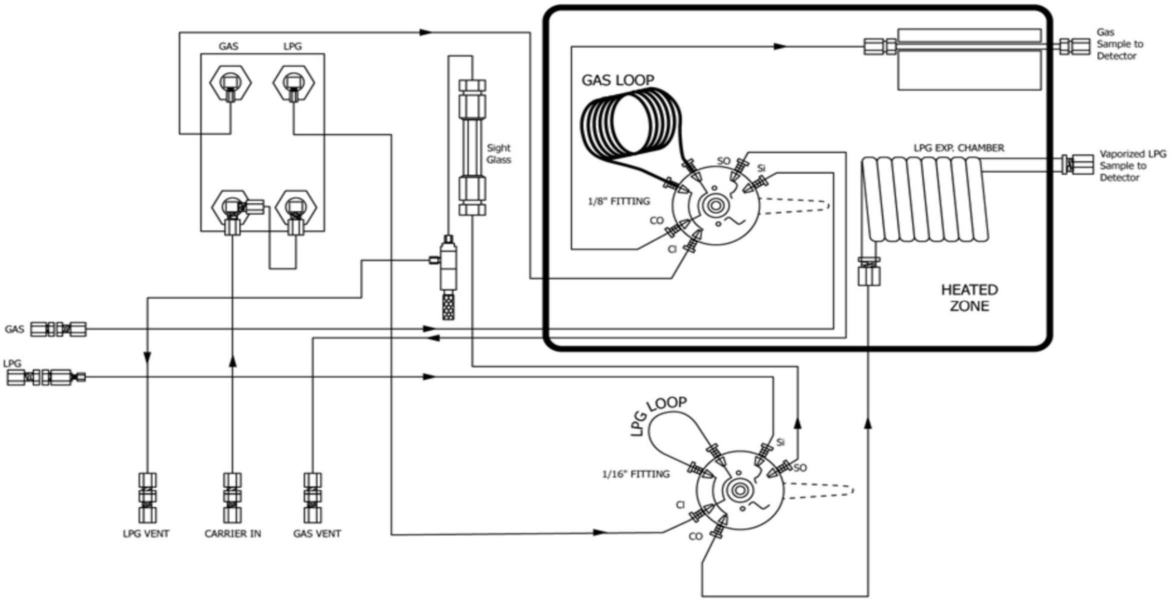

FIG. 3 SAMPLE INLET SYSTEM FLOW PATH

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 specified otherwise, only “Analytical Grade” chemicals shall be used for testing. It need to be ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

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

6.3 Magnesium Perchlorate Mg $(ClO_4)_2$ — For drying products of combustion (permeation drier is not used.)

6.4 Inert Gas — Helium or Argon (Ultra high pure i.e. chromatography or zero grade), 99.998 percent min purity, moisture 5 mg⁄kg max.

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

6.5 Oxygen — 99.75 percent minimum high purity i.e. chromatography or zero grade, moisture 5 mg/kg max, dried over.

6.6 Calibration Standards

Certified Calibration Standards/ Certified Reference Materials (CRMs) from commercial sources or calibration gases prepared using certified permeation tube devices are required. Table 1 lists the Sulphur source material and diluent matrices used during the inter-laboratory study.

Table 1
(*Clause* 6.6)

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

Other sulphur sources and diluent materials may be used if precision and accuracy are ensured and maintained.

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 can 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, or GPA 2174 or GPA 2166 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)

Sl.No.	**Components**	**Conditions**
(1)	**(2)**	**(3)**
i)	Sample inlet system temperature	85 °C ± 20 °C
ii)	Sample injection system carrier gas	25 mL/min to 30 mL/min
iii)	Furnace temperature	1075 °C ± 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 or as per OEM recommendation

Adjust instrument sensitivity and baseline stability and perform instrument-blanking procedures following manufacturer's guidelines.

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 Table 3 and select a calibration range based on the anticipated sulphur concentrations present in samples to be analysed, preferably using a sulphur compound and a diluent type representative of the samples to be analysed (refer note below). Table 3 is representative of typical ranges, but narrower ranges than those indicated may be used if desired. However, the method precision using narrower ranges than those indicated has not been determined. Ensure the standards used for calibration bracket the concentrations of the samples being analysed.

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. autosampler/ 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 LPG samples, if bubbles are present in the visible portion of the liquid column, flush the sample loop to introduce a new liquid-full sample portion.

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

10.5 Calibrate the instrument using one of the following techniques.

10.5.1 *Multi-point Calibration*

10.5.1.1 When the apparatus features an internal self-calibration routine, analyse the calibration standards and blank three times using the procedures described in 10.2 – 10.4.

10.5.1.2 Calibrate the analyser according to the manufacturer's instructions to produce Sulphur concentration (*see* Section 14). This curve is typically linear and system performance shall be checked at least once per day or each use/running day.

> 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 close to that of the samples under analysis (± 25 percent max.).

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

10.5.2.3 Perform measurements of the calibration standard a minimum of three times.

10.5.2.4 Calculate a calibration factor K, in counts per nanogram of sulphur (counts/ng S) as described in 12.2.

11 PROCEDURE

11.1 Collect a test sample using the procedure described in Section 7. Usually the sulphur concentration in the test sample is less than the concentration of the highest standard and greater than the concentration of the lowest standard employed in the calibration.

11.2 Measure the response for the test sample using one of the procedures described in 10.2 – 10.4.

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

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 coked or sooted parts according to the manufacturer's instructions. After any cleaning or adjustment, assemble and check the apparatus for leaks. Repeat instrument calibration prior to reanalysis of the test sample.

11.5 To obtain one result, measure each test sample three times and calculate the average detector response.

11.6 Density values needed for calculations are to be measured using Test Methods D1070/IP 432/ISO 8973/ ASTM D2598 or equivalent or calculate according to 12.2.3, at the temperature at which the sample was 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 (*see* 12.2 – 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 (*see* 12.5 – 12.7).

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

12.2.1 Interconversion to Liquid Volume% from Mass% According to Practice D2421

$$Liquid\ Volume\ \%_x = 100 \times \frac{(\mathrm{Mass\%}_x / Relative\ Density_x)}{\sum_{N=1}^{\#comp} (\mathrm{Mass\%}_n / Relative\ Density_n)} \quad \text{.......(1)}$$

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 D2421, Table 2, Column 3) given for each identified component x as a liquid,

Mass%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% divided by the relative density for all identified components.

12.2.2 Interconversion to Liquid Volume% from Mole% according to practice D2421

$$Liquid\ Volume\%_x = 100 \times \frac{(Mole\%_x \times Volume\ Ratio_x)}{\sum_{N=1}^{\#comp} (Mole\%_n \times Volume\ Ratio_n)} \quad \text{.......(2)}$$

where

Liquid Volume %x = liquid volume% 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 D2421, Table 2, Column 2) given for each identified component x,

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

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

12.2.3 *Relative Density Calculation According to Practice D2598*

$$\text{Relative Density}_{\text{mix}} = \sum_{x=1}^{\#\infty mp}\left(\frac{Liquid\ Volume\%_x \times Relative\ Density_x}{100}\right)$$

……. (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 %x = liquid volume% of all identified components in the sample of which x is one, and

$\sum_{n=1}^{\#\infty mp}$ = 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:

$$\text{Sulphur, mg/kg} = \frac{G \times d}{s} \qquad \text{---- (4)}$$

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 = Ac/ Mc x Scg ---- (5)

Or

K = Ac/Vc x Scv ---- (6)

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 x Dc ---- (7)

where

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

Vc = volume of calibration standard injected, µL,

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

$$S = A/M \times K \times Fg \text{ ----} \qquad (8)$$

Or

$$S = A/V \times K \times Fv \text{ ----} \qquad (9)$$

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.

$$M = V \times D \text{ ----} \qquad (10)$$

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) % from mass % according to Practice D2421:

$$Mol\%_x = 100 \times \frac{\left(Mass\%_x / Molecular \quad Mass_x\right)}{\sum_{n=1}^{\#comp} \left(Mass\%_n / Molecular \quad Mass_n\right)} \quad \text{---(11)}$$

where

Mol%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 D2421, Table 2, Column 1) given for each identified component x,

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

$\sum_{n=1}^{\#\infty mp}$ = the sum of the quotients Mass% divided by the molecular mass for all identified components.

12.5.2 Calculation of the mole mass of the mixture:

$$Molecular\ \ Weight_{mixture}\,(g\,/\,mol) = \frac{(x_1 \times M_1 + x_2 \times M_2 + \ldots x_n \times M_n)}{100} \quad \ldots\ldots\ldots\ldots(12)$$

where

x = mole% 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:

$$\text{Sulphur (mg/kg)} = \frac{G \times Molecular\ Mass_x}{Molecular\ Mass_y} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(13)$$

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).

$$K = Ac/\ mc \times Scg \ldots\ldots\ldots\ldots\ldots\ldots(14)$$

Or

$$K = Ac\ /\ Vc \times Scv \ldots\ldots\ldots\ldots\ldots\ldots(15)$$

where

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

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

$$mc = V \times \text{Molecular Mass } x \ldots\ldots\ (16)$$

where

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

Vc = volume of calibration standard injected, µL,

Scg = Sulphur content of calibration standard, mL/kg, and

Scv = 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:

$$S = A/m \times K \times Fg \text{ …………}(17)$$

Or

$$S = A/V \times K \times FV\text{…………}(18)$$

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.

$$m = V \times \text{Molecular Mass } y\text{………}(19)$$

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,

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.

NOTE — Calculation examples are described in Appendix A4.

13 REPORT

13.1 For results equal to or greater than 10 mg ⁄kg, report the sulphur results to the nearest mg/kg. For results less than 10 mg ⁄kg, report the sulphur results to the nearest 0.1 mg ⁄kg. State that the results were obtained according to Test Method D6667.

14 QUALITY CONTROL

14.1 Confirm the performance of the instrument or the test procedure by analysing a Quality Control (QC) sample (refer 6.7) after each calibration and at least each day of use thereafter (refer 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, Appendix A1 can 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:

$$r = 0.1152\ (X)\text{ ………..}(8)$$

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

$$r = 0.2707\,(X)^{0.7} \ldots\ldots\ldots\ldots(9)$$

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:

$$R = 0.3130\,(X) \ldots\ldots\ldots\ldots(10)$$

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

$$R = 2.3205\,(X)^{0.7} \ldots\ldots\ldots\ldots(11)$$

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)

SI No. (1)	Concentration	Repeatability		Reproducibility	
	S (mg/kg) (2)	Gaseous Hydrocarbons (3)	LPG (4)	Gaseous Hydrocarbons (5)	LPG (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[A]	9	N/A	77
vii)	196	N/A	11	N/A	93

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

ANNEX A

(Non-mandatory Information)

A-1 QUALITY CONTROL MONITORING

A-1.1 Confirm the performance of the instrument or the test procedure by analysing Quality Control (QC) sample(s).

A-1.2 Prior to monitoring the measurement process, the user of the test method needs to determine the average value and control limits of the QC sample. Practice ISO 4259/IS 17371/ ASTM D6299 and MNL7 (MNL 7, Manual on Presentation of Data Control Chart Analysis, 6th Ed., Section 3, ASTM International) may be referred.

A-1.3 Record the QC results and analyse by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process. Refer Practice ISO 4259/IS 17371/ ASTM D6299 and MNL7. Investigate any out-of-control data for root cause(s). The results of this investigation may, but not necessarily, result in instrument re-calibration.

NOTE — A-1.1—In the absence of explicit requirements given in the test method, A1.4 provides guidance on QC testing frequency.

A-1.4 The frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements.

Generally, a QC sample should be analysed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analysed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample testing precision should be periodically checked against the ISO/IS/ASTM method precision to ensure data quality. See Practice ISO 4259/IS 17371/ ASTM D6299 and MNL7.

A-1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analysed. An ample supply of QC sample material should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions.

A-1.6 See Practice ISO 4259/IS 17371/ ASTM D6299 and MNL7 for further guidance on QC and control charting techniques.

A-2 OPERATION SUGGESTIONS AND SAFETY ASPECTS

A-2.1 Fully stabilise and ready the apparatus for analysis according to the manufacturers' instructions before sample injection.

A-2.2 Valves in the sample inlet system typically remain in the load position except during sample analysis.

A-2.3 Once the sample valve has been filled and equilibrated, complete sample injection by executing a prompt and full rotation to the sample valve to the inject position.

A-2.4 Leave the sampling valve in the inject position until analysis has completed (instrument baseline is achieved and integration is completed.)

A-2.5 The length of time required for detector response depends upon the type of pyrotube utilized, carrier gas, sample size or sulphur concentration, or both. From 20 s to 1 min can be typical (refer Fig. A2.1).

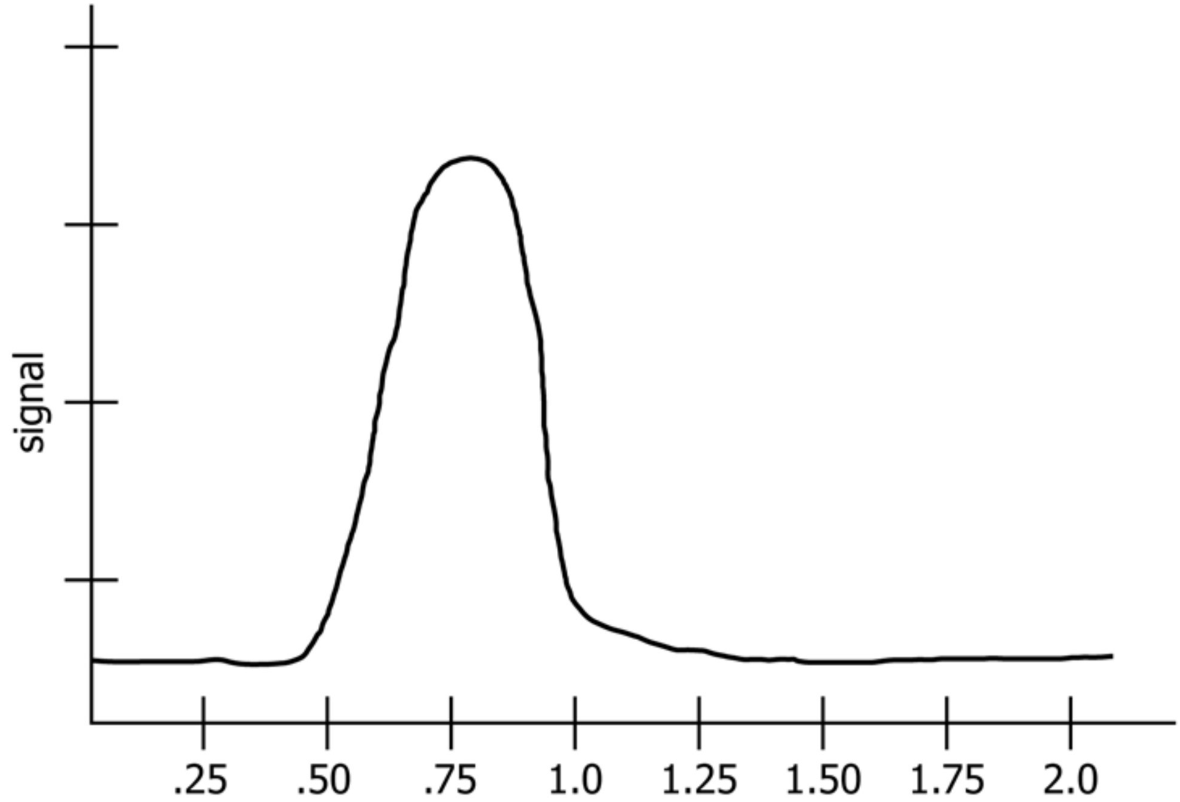

FIG. A-2.1 Typical Injection Profile

A-2.6 Sample inlet system carrier gas flows can be used to control sample combustion and detection characteristics. However, excessive carrier flow rates (greater than 30 mL ⁄min) can cause incomplete sample combustion which may result in sooting.

A-2.7 Allow time for return of signal to baseline between injections.

A-2.8 For sample cylinders containing liquefied petroleum gases, use sufficient pressure (typically greater than 200 psig container pressure) to allow the transfer of sample to the sample inlet system without the formation of bubbles in the transfer tubing and sight glass.

A-2.9 Use standard gas flow conditions for analyser as per requirement. See Section 9 of the test method.

A-2.10 The use of a filtering device prior to sample introduction is strongly recommended. This can greatly extend valve service and prevent transfer line (tubing) blockage.

A-2.11 The use of low or iron-free alloys and/or inert treated materials can enhance the analysis for low level sulphur concentration.

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 transfer lines and fittings used to connect the sample container to the sample inlet system for leaks and stress weakening that can be caused by frequent bending, age, or use.

A-3.2 Check Quick-Connect fittings/couplings and other sample transfer and venting apparatus routinely for leaks and proper operation.

A-3.3 Vent waste gases from the sample inlet system to an area away from the instrument operating environment and potential ignition sources.

A-3.4 Pressures applied to maintain contents of sampling cylinders and to enable sample transfer are typically less than 750 psig. Do not exceed the general overall pressure rating (900 psig) of the sample inlet system or the capacity of the sample transfer apparatus being applied.

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 sample loop loading, allow pressure within the loop and vent system to equilibrate. Use of a secure gas-bubble monitoring device that vents to an area free of potential ignition sources can provide visual confirmation and aid in ensuring the injection of consistent sample sizes.

A-3.7 After sampling is complete, a controlled venting or relief of pressure of the sample transfer line is advised.

A-3.8 After analysis, with the sample valves in the load position, an inert gas connected to the sample inlet system can be utilized to purge 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 – 12.4.

A-4.1.1 *Step 1—Interconversion to Liquid Volume%*—A sample calculation using the hypothetical LPG compositional analysis is given in Table A4.1.

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

$$\sum_{x=1}^{\#comp} \times \left(\frac{Liquid\ \ Vol\%_x \times Relative\ \ Density_x}{100} \right) =$$

$$\text{Relative Density} = \frac{(0.07 \times 0.35639) + (80.57 \times 0.50736) + (5.09 \times 0.56293) + (14.27 \times 0.58407)}{100}$$

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.

Corrected result = 0.5842/0.5210 x 50 = 56 mg⁄kg (A4.2)

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

Table A-4.1 Conversion from Mass% to Liquid Vol% for Selected Properties

Sl. No.	LPG	Mass%	Mass% Relative Density (kg/m3) a	Quotient Mass% / Relative Density	Liquid Vol% (V/V%) Multiply by Normalization Factor
(1)	(2)	(3)	(4)	(5)	(6)
i)	Components	0	0.3	0	0
ii)	Methane	0.05	0.35639	0.14	0.07
iii)	Ethane	78.45	0.50736	154.624	80.57
iv)	Propane	5.5	0.56293	9.77	5.09
v)	Isobutane	16	0.58407	27.394	14.27
vi)	N butane	100		191.928	100

A Source: Practice D2421, Table 2, Col 3.

A-4.2.1 *Step 1 — Interconversion to Mole%*—A sample calculation using the hypothetical LPG compositional analysis is given in Table A4.2 column 1 and 2. The results of the conversion from mass% to mole% is shown in Table A4.2 column 3 to 5.

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

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

$$= 46.50$$

A4.2.3 *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.

Corrected result = 58.12/46.5 x 50 = 62 mg⁄kg (A4.4)

Table A-4.2 Conversion of Mass% to Mole% for Selected Properties

Sl. No.	LPG Components	Mass%	Mass% Relative Density (kg/m3) A	Quotient Mass% / Relative Density	Liquid Vol% (V/V%) 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)	N butane	16	58.12	0.2753	12.8
vi)	Total	100		2.1507	100

A Source: Practice D2421, Table 2, Column 1.
B Normalization factor is calculated by 100 divided by the sum of all the individual quotients in Column 4.