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Natural gas — Determination of sulfur compounds — Determination of total sulfur by oxidative microcoulometry method

Gaz naturel — Détermination des composés soufrés — Détermination de la teneur totale en soufre par microcoulométrie oxydante

Reference number
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Foreword

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The committee responsible for this document is ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*.

Introduction

Three methods for determination of sulfur compounds in natural gas already exist as International Standards:

- ISO 6326-3, Natural gas — Determination of sulfur compounds — Part 3: Determination of hydrogen sulfide, mercaptan sulfur and carbonyl sulfide sulfur by potentiometry;
- ISO 6326-5, Natural gas — Determination of sulfur compounds — Part 5: Lingener combustion method;
- ISO 19739, Natural gas — Determination of sulfur compounds using gas chromatography.

Natural gas — Determination of sulfur compounds — Determination of total sulfur by oxidative microcoulometry method

WARNING — The use of this International Standard can involve hazardous material, operations, and equipment. This International Standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this International Standard to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard specifies a method for the determination of total sulfur in the range from 1 mg/m^3 to 200 mg/m^3 in pipeline natural gas by oxidative microcoulometry. Natural gas with sulfur contents above 200 mg/m^3 can be analysed after dilution with a suitable sulfur-free solvent.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 6142, *Gas analysis — Preparation of calibration gas mixtures — Gravimetric method*

ISO 6144, *Gas analysis — Preparation of calibration gas mixtures — Static volumetric method*

ISO 6146, *Gas analysis — Preparation of calibration gas mixtures — Manometric method*

ISO 10715, *Natural gas — Sampling guidelines*

3 Test principle

A gas sample containing sulfur is mixed with oxygen in a quartz furnace tube in order to convert the sulfur compounds to sulfur dioxide by oxidative pyrolysis. The obtained sulfur dioxide enters the titration cell along with carrier gas and reacts with iodine contained therein. The consumed iodine is complemented by the electrolysis of potassium iodide. In accordance with Faraday’s law of electrolysis, the sulfur concentration in the gas sample can be calculated from the consumed electric quantity by electrolysis and corrected by comparison to a reference standard sample.

4 Reagents

4.1 Test water, conforming to the requirements of Grade 3 of ISO 3696,

4.2 Glacial acetic acid, analytical purity.

4.3 Potassium iodide, analytical purity.

4.4 Oxygen, minimum purity 99,99 % (by volume fraction), maximum volume fraction of sulfur containing gases 0,01 % (by volume fraction).

4.5 Carrier gas, argon, helium, or nitrogen with a minimum purity 99,99 % (by volume fraction), maximum volume fraction of sulfur containing gases 0,01 % (by volume fraction).

5 Apparatus

5.1 Converter

There are three independent heating sections in a converter: preheating section (800 °C ± 20 °C), combustion section (900 °C ± 20 °C), and exit section (800 °C ± 20 °C).

5.2 Titration cell

Install a pair of electrolysis electrodes and a pair of indicator-reference electrodes in the cell.

5.3 Microcoulometer

Electrolysis commences automatically when there is a reduction in the concentration of iodine caused by the presence of sulfur dioxide in the titration cell, to maintain the concentration of iodine at its original level. The microcoulometer can automatically record the electrolysis time and current and directly display the sulfur content.

5.4 Flow controller

Provides the specified flow rates at the outlet.

5.5 Electromagnetic agitator

Provides the specified rotational rates in the titration cell.

5.6 Medical syringe

Air tight syringes of volumes 0,25 ml, 1 ml, 2 ml, and 5 ml. Syringe-delivered volumes should be calibrated by weighing pure water prior to initial use. Periodic calibration might be required thereafter.

5.7 Volumetric flask

One standard laboratory volumetric flask of nominal 25 ml volume.

6 Test preparation

6.1 Preparation of electrolyte

Weigh 0,5 g potassium iodide, dissolve it in 100 ml water, add in 5 ml glacial acetic acid, and then dilute the solvent to 1 L with water. The electrolyte should be stored in a brown reagent bottle. The electrolyte shelf life after preparation is three months.

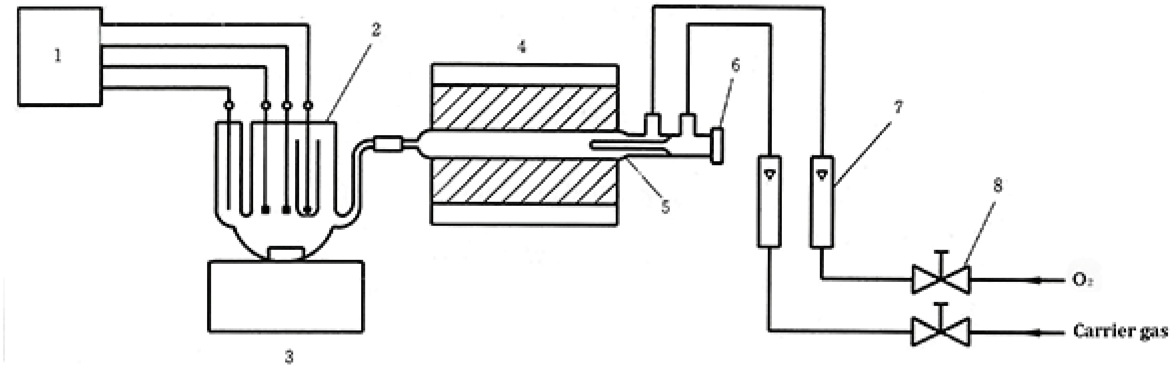
6.2 Reference sample

Use calibration gas mixtures of sulfur compounds prepared according to ISO 6142, ISO 6144, or ISO 6146. Sulfur concentration in the calibration gas mixtures shall be close to that in the tested sample.

It is recommended that sulfur compounds in the calibration gas mixture were hydrogen sulfide (H_2S) in a methane matrix.

6.3 Apparatus installation

Install the apparatus following the instruction. Connect the carried gas tube and oxygen tube. An example of a typical microcoulometer set-up is given in Figure 1.



Key

1 microcoulometer
2 titration cell
3 electromagnetic stirrer
4 reforming furnace
5 quartz furnace tube
6 injection port
7 flow meter
8 needle valve

Figure 1 — Typical microcoulometric set-up

6.4 Preparation of instrument

Replace the silicone rubber plug in the injection port. Regulate the flow rate of carrier gas and oxygen to the values specified by the apparatus. Then switch on the electromagnetic stirrer, adjust stirring speed to produce a slight vortex in the electrolyte

6.5 Check and adjustment of the instrument

Check and adjust all the operating parameters according to the instruction manual of the instrument.

6.6 Determination of recovery factor of sulfur

Install software of microcoulometer and display the sulfur recovery factor using computer software, typically installed on a person computer (PC), suited for the microcoulometer being used.

6.6.1 Sampling and injection

Take samples after flushing the syringe with the gas standard sample four to five times. The syringe plunger should be pushed to the required scale by the gas pressure in the bottle when sampling. Insert the syringe into the injection port, the injection rate is about 0,15 ml/s to 0,2 ml/s and the injection volume is typically 0,25 ml to 5 ml.

6.6.2 Measurement

Switch the instrument to correction factor mode. Enter the concentration of the standard sample and the injection volume. Carry out the determination of the microcoulometer recovery factor by injecting a standard sample according to the method described in 6.6.1. The sulfur recovery factor displayed on the instrument can be used when the relative standard deviation of five consecutive recovery factors is equal or less than 2 %, take the average of these five consecutive values as the recovery factor of the instrument used for measurements.

In case the recovery factor is less than 75 % (F in Formula (3), 2 decimal places), it is necessary to identify the reason[2][3].

7 Test procedure

7.1 Sampling

7.1.1 Sampling from natural gas pipeline

Sampling shall be performed in accordance with ISO 10715.

7.1.2 Sampling from gas cylinders

Analysis should be performed as soon as possible after receiving the samples. Sampling shall be performed in accordance with 6.6.1.

7.2 Sample injection and measurement

Switch the instrument to sample measurement mode. Input volume parameters into the microcoulometer software (corrected to reference conditions). Carry out the determination of the sample recovery factor by injecting the sample according to the method described in 6.6.1. The sulfur recovery factor displayed on the instrument can be used. The sulfur recovery factor and the sulfur mass of the sample can be displayed on the instrument. Carry out the measurement twice, taking the average of the two measurement results.

8 Calculation

8.1 Volume conversion

8.1.1 Volume of gas sample on a dry basis

Volume of gas sample on a dry basis is calculated by Formula (1):

$$V_\mathrm{n} = V\frac{P - P_\mathrm{v}}{P_\mathrm{ref}} \times \frac{T_\mathrm{ref}}{273{,}15 + T} \qquad (1)$$

where

V_n is the calculated volume of the gas sample, ml;

V is the injection volume, ml;

P is the laboratory pressure,kPa;

P_ref is the reference pressure, kPa;

T_ref is the reference temperature, K;

P_v is the water vapour partial pressure in gas sample,kPa;

T is the laboratory temperature, °C.

NOTE Usually reference values of P_{ref} = 101,325 kPa and T_{ref} = 288,15 K are taken[1].

Values of P, P_{ref}, and P_v shall be quoted with three digits after the decimal point, values of T_{ref} and T shall be quoted with two digits after the decimal point, values of V_n and V shall be quoted with one digit after the decimal point.

8.1.2 Volume of gas sample on a wet basis

Volume of gas sample on a wet basis is calculated by Formula (2):

$$V_n = V \frac{P}{P_{ref}} \times \frac{T_{ref}}{273{,}15 + T} \qquad (2)$$

where

V_n is the calculated volume of the gas sample, ml;

V is the injection volume, ml;

P Is the laboratory pressure,kPa;

P_{ref} is the reference pressure, kPa;

T_{ref} is the reference temperature, K;

T is the laboratory temperature, °C.

NOTE Usually, reference values of P_{ref} = 101,325 kPa and T_{ref} = 288,15 K are taken[1].

Values of P and P_{ref} shall be quoted with three digits after the decimal point, values of T_{ref} and T shall be quoted with two digits after the decimal point, values of V_n and V shall be quoted with one digit after the decimal point.

8.2 Calculation of total sulfur mass concentration in the gas sample

The total sulfur mass concentration (as S) in the gas sample is calculated by Formula (3):

$$S = \frac{m \times 10^6}{V_n \times F} \qquad (3)$$

where

S is the total sulfur mass concentration in the gas sample, mg/m^3;

m is the measured mass of total sulfur, mg;

V_n is the calculated volume of the gas sample, ml;

F is the sulfur recovery factor, %.

Values of S, m, V_n, and F shall be quoted with one digit after the decimal point.

9 Precision

9.1 General

The precision of test results on a matrix of samples with sulfur contents in the range of 1 mg/m^3 to 200 mg/m^3 is given in 9.2.

9.2 Repeatability

Under repeatability conditions, the difference of two test results in a short time interval should not exceed the values listed in Table 1 at a 95 % level of confidence

Table 1 — Repeatability of different concentration ranges mg/m^3

Concentration ranges	Repeatability limits
1 to 14	0,6
14 to 100	4,2
100 to 200	9,2

Bibliography

[1] ISO 13443, *Natural gas — Standard reference conditions*

[2] ASTM D 3246, *Standard test method for sulfur in petroleum gas by oxidative microcoulometry*

[3] GB/T 11060.4, *Natural gas — Determination of sulfur compound— Part 4: Determination of total sulfur content by oxidative microcoulometry method*

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