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Natural gas — Determination of sulfur compounds — Determination of total sulfur content by ultraviolet fluorescence method

Gaz natural — Détermination des composés soufrés — Détermination de la teneur en soufre total par la méthode par fluorescence UV

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Foreword

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This document was prepared by Technical Committee ISO/TC 193, *Natural gas,* Subcommittee SC 1, *Analysis of natural gas.*

Introduction

Four 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*;
- ISO 16960, *Natural gas — Determination of sulfur compounds —Determination of total sulfur by oxidative microcoulometry method*.

Ultraviolet fluorescence method is more efficient method compared with potentiometry, because it can measure the result value at once. It is also environment friendly compared with potentiometry, Lingener and oxidative microcoulometry methods which use toxic and hazardous reagents. Moreover, it is much more convenient and stable than existing natural gas total sulfur analysis method, because the method is sensitive to less number of interference factors.

Natural gas — Determination of sulfur compounds — Determination of total sulfur content by ultraviolet fluorescence method

WARNING — The majority of sulfur compounds are extremely toxic and thus present a serious health hazard if handled without precautions.

1 Scope

This method applies to the determination of total sulfur content in natural gas expressed as sulfur mass concentration ranging from 1 mg/m^3 to 200 mg/m^3. 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 are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 6141, *Gas analysis — Requirements for certificates for calibration gases and gas mixtures*

ISO 10715, *Natural gas — Sampling guidelines*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

3.1
absorption
extraction of one or more components from a mixture of gases when brought into contact with a liquid

3.2
adsorption
retention, by physical or chemical forces of gas molecules, dissolved substances, or liquids by the surfaces of solids or liquids which they are in contact

3.3
sorption
process in which one substance takes up or holds another (by either absorption or adsorption)

4 Test conditions

The test conditions are the same as the calibration conditions.

The reference conditions of the measurement results are the same as those on the calibration gas certificates.

NOTE The reference conditions on the calibration gas certificates usually are 101.325 kPa, 20 °C or 101.325 kPa, 15 °C or 101.325 kPa, 0 °C

5 Principle of the method

Typical gas samples are injected by sampling system into a high temperature combustion tube where sulfur is oxidized to sulfur dioxide (SO_2) in an oxygen-enriched atmosphere. The combustion gases are then exposed to ultraviolet (UV) light which causes the SO_2 to be converted to excited SO_2* after absorbing energy from the UV light. Fluorescence emitted from the excited SO_2* as it returns to ground state is detected by a photomultiplier. The resultant signal is a measure of the sulfur content in the sample (see Figure 1.)

6 Instruments

6.1 The main components of the instruments are shown in Figure 1.

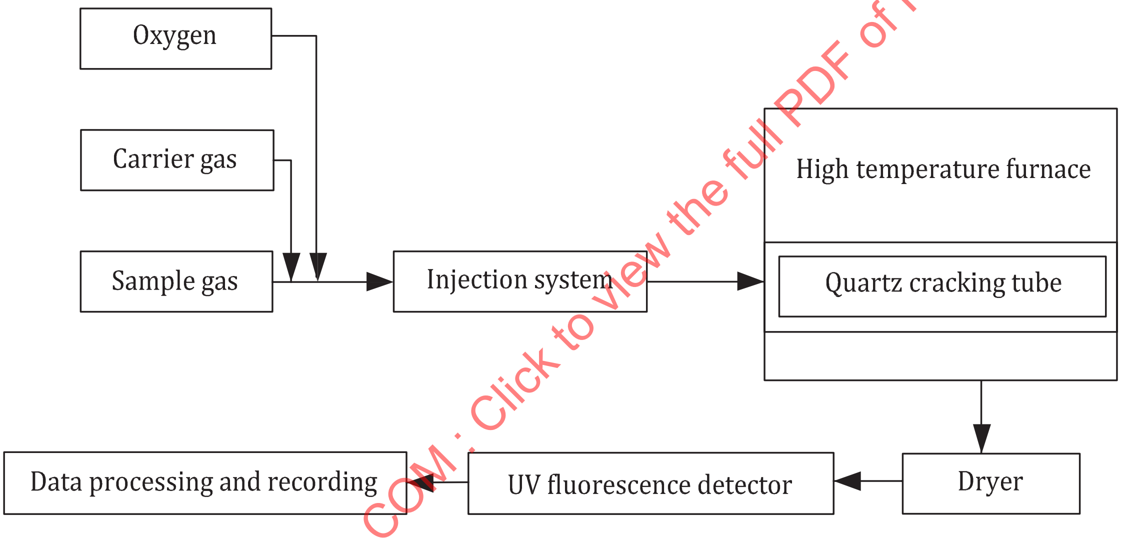

Figure 1 — Schematic diagram of the ultraviolet fluorescence instrument

6.2 Injection system, providing a stable flow of carrier gas and sample gas and can control the injection port open or closed. Sample volume, flow rate and pressure are determined according to the instrument operation specification.

6.3 High temperature furnace, with stable temperature maintained at 1 000 °C ± 50 °C. This temperature is sufficient to pyrolyze the entire sample and oxidize sulfur to SO_2.

6.4 Quartz cracking tube

The sample is directly injected into the heated oxidation zone of the furnace, and mixed with oxygen, which ensures complete combustion of the sample. The quartz cracking tube may have bypasses in order to inject oxygen and carrier gas.

6.5 Dryer, which is used to remove the water vapour formed during sample combustion. This can be achieved by a membrane drying tube, or an osmotic dryer which removes water by selective permeation.

6.6 UV fluorescence detector, a quantitative detector which can measure the fluorescence emitted from SO_2 by UV light.

6.7 Data processing and recording apparatus, recorder or equivalent electronic data recording apparatus, integrator, computer.

7 Reagents

7.1 Carrier Gas, argon or helium with purity of not less than 99,99 % (by volume fraction).

NOTE Nitrogen is not selected to avoid the formation of nitrogen oxygen compounds under electric discharge or high temperature.

7.2 Oxygen, whose purity is not less than 99,99 % (by volume fraction).

NOTE Air is not selected to avoid the formation of nitrogen oxygen compounds under electric discharge or high temperature.

7.3 Calibration gases, which perform regular calibration using working standard gas mixtures certified in accordance with ISO 6142 or with ISO 6144 or with ISO 6145. The working standard gas mixtures shall contain appropriate concentrations and cover the analytic range of the analyser. And the mixtures should be either H_2S in nitrogen or methane or COS in nitrogen or methane.

A certificate of mixture according to ISO 6141 should always be available with the cylinder.

8 Sampling

Sampling shall be performed in accordance with ISO 10715.

All the materials used for sampling equipment and transfer lines shall be inert to sulfur compounds. For direct sampling, it should include sample conditioning to ensure the gas injected into the analysis unit does not contain any liquid water, dust or liquid hydrocarbons.

NOTE Due to the strong tendency of sulfur compounds to be adsorbed by different materials, it is important to purge the instrument and all the surfaces from the cylinder valve to the injection point for 30 s to 2 min with the sample gas before the analysis, in order to avoid sorption effects with different samples or with the calibration mixture.

9 Sample analysis

9.1 Preparation of instrument

Open the valve of the carrier gas and oxygen cylinder then start up the instrument, allow the temperature of the furnace to stabilize at the specified value (1 000 °C ± 50 °C). Check and adjust all the operating parameters according to the manufacturer's instructions.

9.2 Calibration curve

Perform regular calibration using reference gases (see 7.3), that shall be an appropriate number of concentrations of sulfur compounds in methane or nitrogen gas depending upon the estimated sulfur concentration of the sample gas.

Establish a calibration curve using least-square method with at least three different concentrations, inject the reference gas at each concentration at least three times. The linear correlation coefficient of the curve should be not less than 0,998. Example of concentration points are shown in Table 1. If required, narrower ranges may be used.

Table 1 — Examples of sulfur concentrations for a calibration curve

Curve I c_S mg/m^3	Curve II c_S mg/m^3
1,0	60
5,0	100
10,0	130
30,0	170
60,0	200

NOTE Sulfur mass concentration value is obtained by conversion of the H_2S or COS content in the calibration gas mixture.

A calibration curve shall be fitted using linear regression as follows:

$$y = a \cdot x + b \tag{1}$$

where

y is *the* integrated detector response for reference gas, in counts number;

a is the slope of the calibration curve;

x is the total sulfur content of inlet reference gas, mg/m^3;

b is the intercept of the calibration curve.

10 Analysis

10.1 Test

For online analysis, only one measurement is made because of the change of the pipeline gas composition with time; for offline analysis, at least three times for each sample tested are recommended. The difference between two successive results shall not exceed the limit of repeatability (See Table 2).

10.2 Calculation

Inject the sample gas under the same test conditions of the reference gas (see 7.3). The detector response value is y_0, and the corresponding total sulfur content is calculated by the following formula:

$$x_0 = \frac{y_0 - b}{a} \tag{2}$$

where

x_0 is the total sulfur content, mg/m^3;

a and b are both obtained through Formula (1) ;

y_0 is the detector response value.

11 Precision

11.1 General

The following data are obtained from inter-laboratory research. The calculations of repeatability and reproducibility are according to ISO 4259.

Example of the statistical analysis of precision experiments is given in Annex A.

11.2 Repeatability

For offline analysis,for one sample, under repeatability conditions, the absolute value of the difference between two successive times test results should not exceed the limit of repeatability shown as Table 2.

Table 2 — Repeatability of different concentration ranges

Total sulfur concentration	Repeatability limits mg/m^3
1 to 6	0,8
above 6 to 20	2,0
above 20 to 100	4,1
above 100 to 200	7,4

11.3 Reproducibility

For offline analysis, for one sample, under reproducibility conditions, the absolute value of the difference between two successive test results should not exceed the limit of reproducibility shown as Table 3.

Table 3 — Reproducibility of different concentration ranges

Total sulfur concentration	Reproducibility limits mg/m^3
1 to 6	1,1
above 6 to 20	2,6
above 20 to 100	5,4
above 100 to 200	11,6

Annex A
(informative)

Example of the statistical analysis of precision experiments

A.1 Background

a) Measurement method

All the laboratories used ultraviolet fluorescence method to determine the total sulfur content, and all the units of the results are mg/m^3, expressed as sulfur.

b) Description

Eight laboratories which came from different companies participated in the comparison experiment. All of the test objects are the same batch of standard gases, include different concentrations of hydrogen sulfide gas mixture in nitrogen and carbonyl sulfide gas mixture in nitrogen.

A.2 Original data

Each sample was tested at least 11 times continuously. Two consecutive values from these results were randomly selected according to ISO 4259. These results are listed in Tables A.1 and A.2, and do not require any specific remarks.

Table A.1 — Original data of sulfur content of hydrogen sulfide

Laboratory	Sample										
	1	2	3	4	5	6	7	8	9	10	11
A	0,94	6,34	19,,02	20,72	39,98	58,69	78,49	100,18	155,69	193,16	194,27
	1,73	5,28	15,33	18,34	42,78	56,99	82,12	103,85	153,13	197,56	198,80
B	2,08	6,50	15,50	22,01	37,54	57,27	81,08	102,33	153,55	187,46	192,79
	1,95	6,29	16,29	20,10	40,82	58,02	79,19	99,64	155,12	191,04	191,30
C	1,59	6,00	15,08	19,61	40,83	60,07	80,27	100,37	151,32	188,54	192,17
	1,76	5,74	15,75	20,21	41,52	59,15	80,97	101,36	152,32	191,12	187,45
D	1,43	5,80	14,50	18,70	38,80	57,10	81,80	102,00	160,00	200,00	198,00
	1,35	5,69	13,80	18,90	36,00	57,80	80,30	98,40	158,00	195,00	193,00
E	1,67	5,89	14,93	20,15	40,7	57,97	88,67	102,1	158,7	190,3	189,97
	1,39	5,79	15,13	19,97	40,41	57,18	83,34	103,46	152,73	188,78	186,86
F	2,37	6,62	15,00	19,71	40,77	61,25	83,12	103,75	154,03	194,79	194,62
	2,55	6,36	15,12	19,21	41,49	61,63	84,31	105,50	150,70	197,31	195,66
G	1,54	5,84	14,80	20,00	39,80	56,00	81,50	100,20	150,50	187,10	190,70
	1,44	5,62	15,10	19,80	37,00	54,90	83,40	103,50	152,20	189,80	188,70
H	1,48	4,32	11,60	18,40	39,80	61,10	80,10	98,20	148,40	184,20	191,80
	1,95	5,65	13,70	20,80	42,20	57,20	83,90	102,40	153,40	192,40	195,70

Table A.2 — Original data of sulfur content of carbonyl sulfide

Laboratory	Sample									
	1	2	3	4	5	6	7	8	9	10
A	1,06	5,24	14,68	19,16	38,20	60,92	79,50	100,44	157,01	208,12
	1,68	6,21	12,93	18,42	36,59	62,81	83,47	104,99	150,91	200,24
B	1,26	5,61	14,72	20,44	40,39	65,16	80,87	104,71	153,23	203,53
	1,39	5,91	15,29	20,84	41,05	64,08	80,17	101,00	153,66	204,76
C	1,72	6,08	15,38	20,41	40,60	64,59	78,42	98,73	144,96	198,07
	1,56	5,92	15,14	20,61	40,78	64,95	79,46	98,37	146,94	196,63
D	1,43	5,62	14,50	19,40	39,10	63,70	80,50	99,50	144,00	200,00
	1,46	5,72	14,80	19,80	38,60	63,00	81,40	101,00	150,00	201,00
E	1,68	5,96	15,34	20,82	40,63	66,13	87,92	111,16	156,60	216,93
	1,39	5,81	15,69	20,58	44,57	66,99	85,38	105,72	163,43	210,63
F	2,21	5,95	14,65	20,09	40,57	64,08	83,04	100,95	154,18	206,97
	2,02	5,75	14,81	19,73	38,30	64,79	81,97	101,61	154,76	209,86
G	1,51	6,03	15,40	20,40	41,00	65,00	79,80	101,00	150,00	197,60
	1,58	5,85	15,00	20,60	40,60	65,80	82,90	99,90	152,00	201,60
H	1,98	6,10	14,90	20,40	40,30	64,10	80,90	101,20	152,90	209,50
	1,91	6,28	15,50	21,00	39,80	66,30	82,50	106,10	155,00	213,,20

A.3 Data processing

a) The reported data of Tables A.1 and A.2 were inspected for outliers by following formulas:

Test the repeatability results of the same sample by Cochran rule.

$$C = \frac{e_{\max}^2}{\sum_{i=l}^{L} e_i^2} \tag{A.1}$$

Test the reproducibility results of the same sample by Hawkins rule.

$$B^* = \frac{\left| m_j - a_{ij} / n_{ij} \right|}{\sqrt{SS}} \tag{A.2}$$

where

L is the number of laboratories;

i is the subscript which represents the No. of lab;

j is the subscript which represents the No. of the sample;

a is sum of two repeat results;

e is difference of two repeat results;

m is the overall mean to the same sample;

SS is the sum of squares of deviations of cell means(a_{ij}/n_{ij}).

b) Standard deviation calculation of Tables A.1 and A.2 according the following formulae:

Repeats standard deviation for sample *j*:

$$d_j = \sqrt{\sum_{i=l}^{L} e_l^2 / 2L} \tag{A.3}$$

Reproducibility standard deviation for sample *j*:

$$D_j = \sqrt{\frac{\sum_{i=l}^{L}\left(\frac{a_i}{2}\right)^2 - \left[\sum_{i=l}^{L}\left(\frac{a_i}{2}\right)\right]^2 / L}{L-1} + \frac{d_j^2}{2}} \tag{A.4}$$

The results of inspection for outliers and standard deviation calculation are shown in Tables A.3 and A.4.

Table A.3 — Data processing of sulfur content of hydrogen sulfide

Sample	mean	uniformity of repeatability, *C*	uniformity of reproducibility, *B**	repeatability standard deviation, d_j	reproducibility standard deviation, D_j
1	1,70	0,6118	0,7650	0,2511	0,4144
2	5,86	0,5643	0,7176	0,4426	0,5561
3	15,04	0,6887	0,6919	1,1098	1,5236
4	19,79	0,3579	0,1541	0,9935	0,9522
5	40,03	0,2614	0,6600	1,6033	1,8840
6	58,27	0,6928	0,6716	1,1714	1,9688
7	82,03	0,4214	0,7461	2,0526	2,4807
8	101,70	0,2590	0,7482	2,0630	2,0756
9	153,74	0,4021	0,7318	2,3537	3,1873
10	191,78	0,4574	0,5656	3,0311	4,3802
11	192,61	0,2502	0,4840	2,4989	3,5363

Table A.4 — data processing of sulfur content of carbonyl sulfide

Sample	mean	uniformity of repeatability, *C*	uniformity of reproducibility, *B**	repeatability standard deviation, d_j	reproducibility standard deviation, D_j
1	1,61	0,6908	0,6751	0,1882	0,3086
2	5,88	0,7855	0,7055	0,2718	0,2550
3	14,92	0,7286	0,7922	0,5123	0,6452
4	20,17	0,3700	0,7583	0,3066	0,7206
5	40,07	0,6369	0,6525	1,2342	1,7776
6	64,52	0,4013	0,7134	0,8682	1,5367
7	81,76	0,4159	0,0472	1,5389	2,4833
8	102,27	0,3212	0,0557	2,3998	3,4405
9	152,47	0,3515	0,1250	2,8802	4,9266
10	204,91	0,4297	0,0475	3,0030	6,2099

When the laboratory number $n = 8$, the repeatability test critical values = 0.7945, reproducibility test critical values = 0.8596. Values $C < 0.7945$ and values $B^* < 0.8596$ in the above two tables, so, the results obtained were effective.