International Standard

ISO 11626

First edition
2024-02

Natural gas — Determination of sulfur compounds — Determination of hydrogen sulfide content by UV absorption method

Gaz naturel — Détermination des composés soufrés — Détermination de la teneur en sulfure d'hydrogène par la méthode d'absorption UV

Reference number
ISO 11626:2024(en)

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Published in Switzerland

Contents

Page

Foreword

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

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Natural gas — Determination of sulfur compounds — Determination of hydrogen sulfide content by UV absorption method

1 Scope

This document describes the test method for the determination of hydrogen sulfide content in natural gas by ultraviolet (UV) absorption method.

This document applies to the determination of hydrogen sulfide content in natural gas, in the range from 1 mg/m^3 to 50 mg/m^3.

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 — Contents of certificates for calibration gas mixtures*

ISO 6142-1, *Gas analysis — Preparation of calibration gas mixtures — Part 1: Gravimetric method for Class I mixtures*

ISO 6143, *Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures*

ISO 6145, *Gas analysis — Preparation of calibration gas mixtures using dynamic methods*

ISO 10715, *Natural gas — Gas sampling*

ISO 12963, *Gas analysis — Comparison methods for the determination of the composition of gas mixtures based on one- and two-point calibration*

ISO 14532, *Natural gas — Vocabulary*

ISO 14912, *Gas analysis — Conversion of gas mixture composition data*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 14532 apply.

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

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

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

5.1 The UV light emitted by the light source is split by a grating or a prism, absorbed by a gas sample and then projected onto a photomultiplier tube. After the photoelectric conversion and amplification of the drawn ultraviolet absorption spectrum, hydrogen sulfide can be quantitatively analysed. The absorbance detected by the receiving unit and the content of hydrogen sulfide in the measured gas conform to Lambert-Beer's law.

5.2 The UV light is delivered from the pulsed light source to the flow cell by a fibre-optic cable. In the flow cell, the continuous natural gas samples interact with the light in an optical path. Hydrogen sulfide absorbs different amounts of light at different wavelengths. The UV light leaves the flow cell after passing through the sample and then goes to the spectrum analyser through the optical fibre. A spectroscopic holographic grating decomposes UV light into continuous wavelengths, focuses each decomposed wavelength on a specific photodiode on the diode array and calculates the hydrogen sulfide content according to Lambert-Beer's law through a built-in algorithm.

5.3 Calculation formula: if the analytical signal is absorbance, the content of hydrogen sulfide is calculated by Formula (1):

$$C_S = \frac{A_S}{A_{ref}} C_{ref} \tag{1}$$

where

C_S is the content of hydrogen sulfide in the natural gas sample, expressed in mg/m^3;

A_S is the absorbance of hydrogen sulfide in the natural gas sample;

C_{ref} is the content of hydrogen sulfide in the calibration gas, expressed in mg/m^3;

A_{ref} is the absorbance of hydrogen sulfide in the calibration gas.

6 Instrument

6.1 General requirements

Choose an instrument with an appropriate measuring range according to the content of hydrogen sulfide in the analysed gas. The instrument shall be regularly maintained to ensure its performance according to the instrument manual. The instrument shall meet the requirements of the work site, including but not limited to, explosion-proof, power supply, airtightness, etc.

6.2 Sample processing system

The sample processing system shall ensure that there is no water, liquid hydrocarbon and particulate matter in the sample. Adjust the sample gas to the injection pressure and temperature required by the instrument, and keep them stable.

6.3 Optical analysis system

The optical analysis system generates a beam of light of a specific wavelength which is passed through the sample, and then analysed by a spectrometer.

6.4 Data processing and recording system

The data processing and recording system can be a recorder or an equivalent electronic data recording device or a computer.

7 Reagents and materials

7.1 Zero gas

Zero gas may be pure methane or nitrogen. The mole fraction of a main component in a zero gas shall not be less than 999 mmol/mol.

7.2 Hydrogen sulfide calibration gas mixture

Use the hydrogen sulfide calibration gas mixture determined by ISO 6142-1, ISO 6143, ISO 6145 or ISO 12963 for regular calibration. The content of the hydrogen sulfide calibration gas mixture shall be appropriate and cover the analysis range. The matrix gas may be methane or nitrogen. The calibration gas mixture supplied in the cylinder shall be accompanied with a certificate according to ISO 6141. When the component content is expressed in the certificate as an amount fraction or volume fraction, it shall be converted to mass concentration according to ISO 14912.

7.3 Hydrogen sulfide absorption solution

The hydrogen sulfide absorption solution is an alkali liquor that needs to be replaced regularly according to the actual hydrogen sulfide analysis process.

8 Sampling

8.1 Installation location

Determine the installation location of sampling probe according to ISO 10715.

8.2 Materials requirement

All materials in the sampling system (including probes, pipelines, valves, containers and other components) shall be inert to sulfur compounds and shall be appropriate to the sample and sampling method to ensure that the sample composition is not changed.

8.3 Online sampling requirement

For online sampling, it shall be ensured that the sample flows continuously without obstruction, enters the sampling system through an appropriate sampling probe, and gets into the detection system for less than 10 s. The absolute pressure of the sample entering the instrument should be controlled between 0,5 MPa and 1,0 MPa.

9 Sample testing

9.1 Instrument status confirmation

Follow the steps below to confirm the instrument status before testing.

a) Install the instrument and check airtightness according to the manufacturer's operating instruction.

b) Switch on the carrier gas, start up the instrument and set the instrument parameters to the specified values.

c) Switch on the zero gas. Calculate the average value of the zero gas responses for five consecutive minutes after the data displayed by the instrument is stable, complete zero-point deduction.

d) For online testing, ensure the normal use of the data transmission protocol between the instrument and the process control station.

e) Ensure that the instrument parameters and test data can be displayed normally.

f) Ensure that when the concentration exceeds the set threshold, the process control station can timely alarm.

9.2 Calibration curve establishment

9.2.1 General

Generally, the instrument only includes single-point calibration function. Users can achieve the analysis data automatically depending on the instrument single-point calibration, or use multi-point calibration to calculate according to actual needs. Single-point calibration applies for constant H_2S content in sample. For non-constant natural gas source with changing H_2S content, users can use multi-point calibration to obtain high detection accuracy. It is recommended to establish a calibration curve regularly, preferably not less than once a month.

9.2.2 Single-point calibration

The user shall choose the calibration method depending on the analytical accuracy that is required. The following are candidate methods and their requirements.

— Single-point exact-match calibration: there shall be no statistically significant difference between the content of the H_2S of the selected calibration gas mixture and the content of the H_2S of the sample gas.

— Single-point through origin calibration: the H_2S content of the selected calibration gas mixture shall be within 90 % to 150 % of the H_2S content of the sample gas.

9.2.3 Multi-point calibration

For hydrogen sulfide analysis with large content fluctuations, three or more hydrogen sulfide calibration gas mixtures of different contents shall be used, and a calibration curve covering hydrogen sulfide content in the sample shall be established according to the least square method. The linear correlation coefficient of the straight line is required to be no less than 0,998.

9.3 Analytical procedure

Switch the instrument to detection mode when testing. Adjust the sample input pressure according to the requirements of the instrument to ensure a stable flow rate. The flow rate variation shall be less than 10 %. Under the condition of no venting pipeline, the tested samples shall be absorbed by the hydrogen sulfide absorption solution which contained in a barrel with good sealing placed next to the instrument before being discharged. After the sample test process is stable, it is recommended to record two sets of data separated by 30 s and take the average value as the reported test result. The effective digits of the final reported data shall be consistent with the value of the hydrogen sulfide calibration gas mixture certificate used to calibrate the instrument. The content of hydrogen sulfide is expressed by mass concentration in mg/m^3.

10 Instrument verification

10.1 During the operation of the instrument, a hydrogen sulfide calibration gas mixture shall be used to verify the accuracy of the test results regularly, preferably not less than once a month. Verify whether the test results of the hydrogen sulfide calibration gas mixture are consistent with the standard value. If there is a difference of 10 % from the standard value, the instrument shall be corrected before continuing the test.

10.2 Quality control shall be performed by professionals who are skilled in operating the instrument workstation and related software.

11 Precision

11.1 Repeatability, *r*

In the analytical range given by this document, under repeatability conditions, the absolute difference of two test results in a short time interval (30 s) should not exceed the values listed in Table 1 at a 95 % level of confidence. Annex A gives an example of the statistical procedure of the repeatability calculation.

Table 1 — Repeatability limits at different contents

Range mg/m^3	**Repeatability limit** mg/m^3
1 to 6	0,07
above 6 to 20	0,11
above 20 to 50	0,29

11.2 Reproducibility, *R*

In the analytical range given by this document, under reproducibility conditions, the absolute difference of two successive test results under reproducibility conditions should not exceed the values listed in Table 2 at a 95 % level of confidence. Annex A gives an example of the statistical procedure of the reproducibility calculation.

Table 2 — Reproducibility limits at different contents

Range mg/m^3	**Reproducibility limit** mg/m^3
1 to 6	0,40
above 6 to 20	1,27
above 20 to 50	3,73

12 Uncertainty evaluation

12.1 Principle

The H_2S content is calculated using Formula (1). The uncertainty of the final result is based on Formula (1) with some mathematical computing.

12.2 Random uncertainty of test results ($u_{rel,As}$)

The random uncertainty of test results is calculated by Formula (2):

$$u_{rel,As} = \sqrt{\frac{\sum_{i=l}^{n} (A_i - \bar{A})^2}{n(n-1)}} \qquad (2)$$

where

$u_{rel,As}$	is the relative standard uncertainty of the absorbance (signal) of the sample;
A_i	is the absorbance (signal) of each test;
$\overline{A}$	is the mean of all the absorbance values in one analysis.

12.3 Uncertainty of calibration signal ($u_{rel,Aref}$)

The uncertainty of the calibration signal is evaluated in the same way as the random uncertainty of the test result.

12.4 Uncertainty of reference material ($u_{rel,Cref}$)

The uncertainty of reference material is provided by the calibration gas mixture certificate.

12.5 Combined uncertainty of reported result ($u_{rel,Cs}$)

The combined uncertainty of the reported result is calculated by Formula (3), in which all uncertainties are relative standard uncertainty.

$$u_{rel,Cs} = \sqrt{u_{rel,As}^2 + u_{rel,Aref}^2 + u_{rel,Cref}^2} \quad (3)$$

12.6 Expanded uncertainty of reported result ($U_{rel,Cs}$)

The expanded uncertainty of the reported result is calculated by multiplying the combined uncertainty of the reported result with the corresponding coverage factor (k). The coverage factor is determined as needed, usually taking the value $k = 2$.

Annex A
(informative)

Example of statistical procedure for estimation of the precision

A.1 Background

In order to test the precision of the method, a series of experiments was designed and carried out. It involved 10 instruments in six laboratories. The instruments used in the experiments are listed in Table A.1.

Table A.1 — Analytical instruments used in the experiments

Instrument	Operation time	Principle
A	2016	See 5.1
B	2017	
C	2018	
D	2018	
E	2014	
F	2014	
G	2014	
H	2020	See 5.2
I	2020	
J	2020	

A total of 15 cylinders of calibration gas were used to test the behaviour of the instruments. All the raw data were processed in order to obtain the precision of the method. All the experiments used H_2S/CH_4 as calibration gas, with methane as balance gas. The different contents of H_2S and related uncertainty are listed in Table A.2.

Table A.2 — Cylinders of calibration gas used in the experiments

No.	Content mg/m^3	Uncertainty (k = 2)
1#	1,43	Rel. 2 %
2#	7,23	Rel. 2 %
3#	14,3	Rel. 2 %
4#	28,8	Rel. 2 %
5#	42,6	Rel. 2 %
6#	57,2	Rel. 2 %
7#	1,00	Rel. 2 %
8#	3,01	Rel. 2 %
9#	5,99	Rel. 2 %
10#	10,0	Rel. 2 %
11#	15,0	Rel. 2 %
12#	20,0	Rel. 2 %

Table A.2 *(continued)*

No.	Content mg/m^3	Uncertainty (k = 2)
13#	23,6	Rel. 2 %
14#	28,2	Rel. 2 %
15#	38,1	Rel. 2 %

A.2 Experiments

Instruments A to G used the 1# to 6# calibration gas, and instruments H to J used the 7# to 15# calibration gas for analysis. A total of 11 tests were performed on each calibration gas, on each instrument.

The following procedure was followed:

— before starting the 11 tests, connect the calibration gas with the instrument, sweep the pipe and instrument for more than 5 min and then read the analytical result every 30 s;

— after completing 11 tests, another calibration gas is used in the test.

A.3 Original data

Each sample was tested at least 11 times continuously. Two consecutive values from these results were randomly selected according to ISO 4259-1. These results are listed in Table A.3 and Table A.4, and do not require any specific remarks.

Table A.3 — Original data of hydrogen sulfide content by using instruments A to G

Instrument	H_2S content of calibration gas mg/m^3					
	1#	2#	3#	4#	5#	6#
A	1,49	7,26	14,22	28,90	42,34	57,36
	1,48	7,23	14,17	29,19	42,54	57,25
B	1,41	7,30	14,15	29,25	42,67	57,27
	1,36	7,27	14,27	29,17	42,87	57,54
C	1,46	7,41	14,97	30,26	44,62	60,10
	1,42	7,53	14,99	30,33	44,73	60,08
D	1,44	7,29	14,58	29,42	42,95	58,37
	1,43	7,36	14,69	29,48	43,18	58,30
E	1,47	7,40	13,99	28,86	42,08	55,75
	1,46	7,36	14,03	28,94	42,13	55,64
F	1,42	7,18	14,34	28,62	42,29	56,81
	1,42	7,18	14,38	28,54	42,17	56,66
G	1,36	6,86	13,75	27,37	40,19	53,95
	1,35	6,82	13,66	27,45	40,45	54,30

Table A.4 — Original data of hydrogen sulfide content by using instruments H to J

Instrument	H_2S content of calibration gas mg/m^3								
	7#	8#	9#	10#	11#	12#	13#	14#	15#
H	1,00	3,01	5,99	10,00	15,01	20,01	23,61	28,21	38,12
	0,99	2,98	5,93	9,99	14,99	19,99	23,58	28,18	38,07
I	1,01	3,04	6,06	10,11	15,17	20,22	23,86	28,51	38,52
	1,02	3,03	6,05	10,08	15,13	20,17	23,80	28,44	38,42
J	1,06	3,21	6,35	10,87	15,96	21,20	25,54	30,52	40,69
	1,07	3,18	6,39	10,80	15,98	21,32	25,57	30,59	40,39

A.4 Data processing

The precision of the method was calculated according to ISO 4259-1. After obtaining all the 11 testing results of each analysis, repeatability standard deviation *d* and reproducibility standard deviation *D* are calculated according to the raw data.

Standard deviation calculation of Table A.3 and Table A.4 was done according to Formulae (A.1) and (A.2):

Repeatability standard deviation for sample *j*:

$$d_j = \sqrt{\sum_{i=1}^{L} e_i^2 / 2L} \tag{A.1}$$

Reproducibility standard deviation for sample *j*:

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

where

d is the repeatability standard deviation;

D is the reproducibility standard deviation;

L is the number of laboratories;

i is the subscript which represents the number of a laboratory;

a is the sum of two repeat results;

e is difference of two repeat results.

The results of inspection for outliers and standard deviation calculation are shown in Table A.5.

Table A.5 — Data processing of hydrogen sulfide content

Sample	H_2S content of calibration gas mg/m³	Mean mg/m³	Repeatability standard deviation, d_j mg/m³	Reproducibility standard deviation, D_j mg/m³
7#	1,00	1,03	0,007 1	0,036 4
1#	1,43	1,43	0,017 9	0,046 5
8#	3,01	3,08	0,017 8	0,106 6
9#	5,99	6,13	0,029 7	0,215 6
2#	7,23	7,25	0,041 7	0,204 2
10#	10,0	10,31	0,013 5	0,481 9
3#	14,3	14,30	0,053 9	0,417 2
11#	15,0	15,37	0,020 0	0,522 3
12#	20,0	20,49	0,053 7	0,679 3
13#	23,6	24,33	0,030 0	1,070 4
14#	28,2	29,08	0,042 2	1,289 7
4#	28,8	28,98	0,091 9	0,881 6
15#	38,1	39,04	0,130 7	1,320 0
5#	42,6	42,52	0,128 0	1,301 0
6#	57,2	57,10	0,132 9	1,897 9

If using linear function to express the relationship of the (d_j, D_j) and H_2S content, see Figure A.1 and Figure A.2.

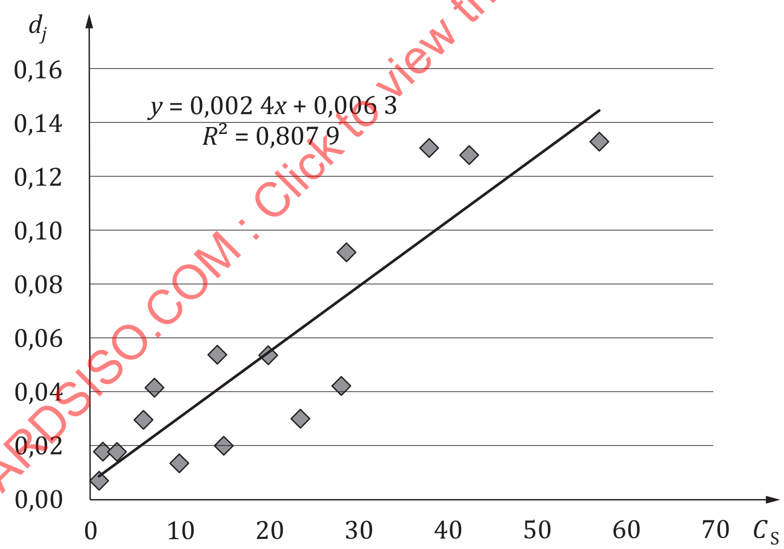

Figure A.1 — Relation between d_j and C_S