ISO/FDIS 11626:2023 (E

ISO<u>/</u>TC 193/SC 1/WG 21

Date: 2023-10-1

Secretariat: NEN

Date: 2023-11-23

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

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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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.

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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 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

 ${\it ISO~6143, Gas~analysis--Comparison~methods~for~determining~and~checking~the~composition~of~calibration~gas~mixtures}$

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 $101,325\,kPa$, $20\,^{\circ}C$ or $101,325\,kPa$, $15\,^{\circ}C$ or $101,325\,kPa$, $0\,^{\circ}C$.

5 Principle

- **5.1** The ultraviolet (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) Formula (1):

$$C_{\rm S} = \frac{A_{\rm S}}{A_{\rm rmf}} C_{\rm ref} \tag{1}$$

$$C_{\rm S} = \frac{A_{\rm S}}{A_{\rm ref}} C_{\rm ref} \tag{1}$$

where

- C_s is the content of hydrogen sulfide in the natural gas sample, expressed in mg/m³;
- 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/m³;
- A_{ref} is the absorbance of hydrogen sulfide in the calibration gas.

6 Instrument Jards.iteh.ai/catalog/standards/sist/bf25e66f-8981-4409-b769-463eefe4b855/iso-fdis-11626

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, air tightness, 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.

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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 sample 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) 1)-Install the instrument and check air tightness according to the manufacturer's operating
 instruction.
- b) 2)—Switch on the carrier gas, start up the instrument and set the instrument parameters to the specified values.
- c) 3)—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) 4)—For online testing, ensure the normal use of the data transmission protocol between the instrument and the process control station.

- e) 5)—Ensure that the instrument parameters and test data can be displayed normally.
- f) 6) 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 H₂S of the selected calibration gas mixture and the content of the H₂S of the sample
 gas.
- Single-point through origin calibration: the H₂S content of the selected calibration gas mixture shall be within 90 % to 150 % of the H₂S 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/m³.

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.