INTERNATIONAL STANDARD

ISO 6326-4

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Natural gas — Determination of sulfur compounds —

Part 4:
Gas chromatographic method using a flame photometric detector for the determination of hydrogen sulfide, carbonyl sulfide and sulfur-containing odorants

Gaz naturel — Détermination des composés soufrés —

Partie 4: Détermination du sulfure d'hydrogène, du sulfure de carbonyle et des composés soufrés malodorants par chromatographie en phase gazeuse avec détecteur à photométrie de flamme

Reference number
ISO 6326-4:1994(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 6326-4 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Sub-Committee SC 1, *Analysis of natural gas*.

ISO 6326 consists of the following parts, under the general title *Natural gas — Determination of sulfur compounds*:

— *Part 1: General introduction*

— *Part 2: Gas chromatographic method using an electrochemical detector for the determination of odoriferous sulphur compounds*

— *Part 3: Determination of hydrogen sulfide, mercaptan sulfur and carbonyl sulfide sulfur by potentiometry*

— *Part 4: Gas chromatographic method using a flame photometric detector for the determination of hydrogen sulfide, carbonyl sulfide and sulfur-containing odorants*

— *Part 5: Lingener combustion method*

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Introduction

The standardization of several methods for the determination of sulfur compounds in natural gas is necessary in view of the diversity of these compounds [hydrogen sulfide, carbonyl sulfide, thiols (mercaptans), tetrahydrothiophene (THT), etc.] and the purposes of the determinations (required accuracy, measurement at the drilling head or in the transmission pipes, etc.).

In order to enable the user to choose the method most appropriate to his needs and to perform the measurements under the best conditions, ISO 6326 has been prepared in several parts.

ISO 6326-1 gives a rapid comparison of standardized methods and therefore provides information for the choice of the method.

The other parts of ISO 6326, including this part, describe in detail the various standardized methods.

The determination of total sulfur is specified in ISO 4260:1987, *Petroleum products and hydrocarbons — Determination of sulfur content — Wickbold combustion method.*

Natural gas — Determination of sulfur compounds —

Part 4:

Gas chromatographic method using a flame photometric detector for the determination of hydrogen sulfide, carbonyl sulfide and sulfur-containing odorants

1 Scope

This part of ISO 6326 specifies a precise and accurate method for the analysis of sulfur compounds in natural gas.

This method is applicable to the determination of hydrogen sulfide, carbonyl sulfide, C1-C4 thiols and sulfides and tetrahydrothiophene (THT), generally in the range 0,5 µmol/mol to 50 µmol/mol. It is also applicable to the quantitative determination of sulfur compounds other than hydrogen sulfide, when hydrogen sulfide is present at concentrations up to 5 000 µmol/mol.

The method uses a single temperature-programmed column, and a sulfur-selective flame photometric detector (FPD).

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this part of ISO 6326. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this part of ISO 6326 are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 6143:1981, *Gas analysis — Determination of composition of calibration gas mixtures — Comparison methods.*

3 Principle

The components are separated using a temperature-programmed oven and a column of styrene/divinylbenzene porous polymer beads and measured with a sulfur-selective flame photometric detector. Potentially interfering hydrobarbons are also separated from the sulfur compounds. Some sulfur compounds are not completely resolved from others. Identification can be aided by selective scrubbing of the sample to remove different types of sulfur compound (see 7.4.2).

4 Materials

4.1 Gases

4.1.1 Carrier gas, nitrogen, helium or argon, [purity > 99,9 % (*m/m*)], free from oxygen and moisture.

4.1.2 Auxiliary gases, hydrogen and oxygen or air, [purity > 99,9 % (*m/m*)].

4.2 Reference materials, individual thiols and sulfides in the range C1 to C4, tetrahydrothiophene, hydrogen sulfide and carbonyl sulfide.

5 Apparatus

5.1 Gas chromatograph, capable of temperature programming and fitted with an FPD.

NOTE 1 The FPD is insensitive to hydrocarbons, and therefore may not register the presence of a hydrocarbon which co-elutes with and, consequently, may quench the response of a sulfur compound. The conditions quoted in this method should avoid such interference for the majority of natural gas compositions. If required, the column effluent can be split between the FPD and a parallel flame ionization detector (FID). The FID will clearly show potential hydrocarbon interference.

5.1.1 Column oven, with a temperature range of 50 °C to 250 °C, capable of being maintained at within ± 0,5 °C at any temperature in the range during an analysis.

5.1.2 Temperature control. The oven shall be provided with a linear programmer suitable for providing a rate of temperature change of 10 °C/min over the specified range.

5.1.3 Flow controller, to supply a suitable carrier gas flowrate.

5.1.4 Pressure controllers and restrictors, to supply suitable auxiliary gas flowrates.

5.2 Injection device, comprising either

- a gas-tight syringe, of capacity 5 ml, constructed of glass and polytetrafluoroethylene (PTFE), or
- a bypass injector, capable of injecting samples from 0,5 ml to 5 ml.

A valve constructed entirely of PTFE is suitable under all circumstances. Certain valves constructed of stainless steel and PTFE have also been found to be suitable. Before use, any such valve shall be tested for possible adsorptive effects on sample components.

5.3 Column: a single column shall be used.

5.3.1 Tube, constructed of glass, perfluoro(ethylene-propylene) (FEP), or any material which has been shown not to absorb sulfur compounds and which is suitable for the temperature range given in 7.1.1.1. The form of the tube is suitable for the chromatograph (5.1).

The tube shall have the following dimensions:

- length: 1,2 m;
- diameter: 2 mm internal or external, depending on the chromatograph;
- radius: suitable for the chromatograph.

5.3.2 Packing

5.3.2.1 Material: styrene/divinylbenzene porous polymer beads, of particle size 150 µm to 180 µm (80 to 100 ASTM mesh).

Before use, the packing shall be washed with acetone to remove soluble impurities.

NOTE 2 This is conveniently carried out by placing a suitable quantity of packing into a sintered filter funnel connected to a vacuum source.

The packing shall be washed with 2 or 3 aliquots of acetone, and then dried by continuing to draw air through it.

After packing, overnight treatment, at approximately 230 °C with carefully dried carrier gas flowing, is necessary for good separation.

5.3.2.2 Method of packing: any method which results in uniform packing may be used.

NOTE 3 The following method is suitable. Close the column outlet with a sintered disc or glass wool plug. Connect a reservoir containing rather more packing than is required to fill this column, to the inlet, and apply a pressure of 400 kPa of nitrogen to the reservoir. The flow of packing into the column may be assisted by vibration. When the column is full, allow the pressure to decrease normally before disconnecting the reservoir. Porous polymer beads often collect static changes, which makes their handling difficult. This effect can be reduced by chilling the batch in a closed container in a refrigerator for several hours before use.

5.3.2.3 Efficiency: when operated under the recommended conditions, the separations shall be similar to, or better than, those shown in figures 1 and 2.

5.3.2.4 Adsorptive behaviour

NOTE 4 Loss of sulfur compounds by adsorption onto surfaces can occur anywhere in the system, not only in the column. Hydrogen sulfide and thiols of low relative molecular mass are most likely to be lost in this way, and therefore the effect can be evaluated by successive injections of a stable gas mixture containing hydrogen sulfide or methanethiol at an appropriate concentration. A gradual increase in peak size with successive injections indicates adsorptive losses. In many cases, such losses can be reduced by injection of commercially available silanizing reagents, such as dimethyldichlorosilane (DMCS).

5.4 Flame photometric detector, operating in the sulfur mode.

If used with an amplifier, the time constant shall be not greater than 0,1 s.

5.5 Potentiometric recorder, with a sensitivity and impedance suitable for the detector or amplifier and a response time not greater than 0,5 s.

5.6 Integrator, with a wide range (1 µV to 1 V), capable of baseline tracking and of measuring peak heights or areas on a sloping baseline.

NOTE 5 The response of the FPD is commonly taken to be proportional to the square of the concentration of a sulfur compound. In fact, the exponent may differ somewhat from 2 and for the most accurate work it should be measured by analysis of suitable standard gases. The exact value can be used to draw up calibration plots or can be inserted into the data handling algorithm.

In fact, the errors arising from using the incorrect exponent are not important. If it is assumed that the exponent is 2, and the real value differs by 10 % relative (i.e. exponent = 1,8 or 2,2) then a difference of × 2 in the concentration of a component in the standard and in the sample will introduce a relative error of 7 %. A difference of × 3 will introduce a relative error of 12 %. If the value of the exponent is incorrect by 20 % relative (i.e. = 1,6 or 2,4), then a difference of × 2 will introduce a relative error of 14 % and a difference of × 3 will introduce a relative error of 25 %.

6 Sample

The natural gas sample shall contain hydrogen sulfide, carbonyl sulfide, thiols, sulfides and/or tetrahydrothiophene individually in the range 0,5 µmol/mol to 50 µmol/mol.

If the sample is taken in a high pressure cylinder, the cylinder shall be non-reactive, internally clean and free from rust and grease. It shall be filled and vented several times to avoid any possibility of contamination by air.

NOTE 6 When the use of aluminium cylinders is permissible according to local regulations, they are more satisfactory than steel ones in terms of resistance to adsorption. Cylinders which have been specially treated internally to minimize adsorption are commercially available. The recommendations in ISO 6326-1:1989, *Natural gas — Determination of sulfur compounds — Part 1: General introduction* should be observed when selecting materials for sampling lines and containers.

7 Procedure

7.1 Control of the apparatus

Set up the gas chromatograph according to the manufacturer's instructions. If the bypass injector is independently heated, set it to 100 °C ± 10 °C. If there is a separately heated inlet zone, set it to 100 °C ± 10 °C.

7.1.1 Oven and column

7.1.1.1 Temperature programme

Set the following temperature programme:

- Initial temperature: 70 °C
- Initial time: 3 min
- Rate: 10 °C/min
- Final temperature: 230 °C
- Final time: 5 min

7.1.1.2 Carrier gas flowrate

Set the carrier gas flowrate so that the hold-up time for methane is approximately 17 s at the initial temperature.

7.1.2 Detector

Set the temperature to between 230 °C and 250 °C. If this causes a high level of noise, set the temperature to a lower value, but not lower than 120 °C.

Adjust the auxiliary gas flows to the values recommended by the manufacturer.

7.1.3 Recorder

Set the chart speed to a minimum of 10 mm/min.

7.1.4 Integrator

Set up the integrator in accordance with the manufacturer's instructions, taking into account note 5 in 5.6. Attenuate the recorder signal, if desired, independently of the integrator input. If quantitative measurements are to be made from the recorder signal, check the actual ratios between the quoted attenuator values.

NOTE 7 If the component concentrations in the standard and sample are similar, they can both be measured at the same attenuation setting.

7.2 Calibration

7.2.1 Method

Use external calibration with standard gas mixtures.

7.2.2 Standard mixtures

7.2.2.1 Prepare a standard mixture of the appropriate sulfur compounds in sulfur-free natural gas of the approximate composition required using any suitable method. Where possible, use a natural gas of similar composition to that expected of the sample from which the sulfur compounds have been removed.

NOTE 8 Such a standard mixture, which is prepared under pressure in a cylinder, can be affected by gradual adsorption of components onto the cylinder walls. Its composition should be checked by an independent method, at intervals of not less than six months.

7.2.2.2 If possible, inject the standard mixture immediately before or after each analysis. If analyses are performed continuously, inject the standard at least twice during a day, once in the morning and once in the afternoon. If analyses are not performed continuously, or the apparatus has not been used for a period of time, for example overnight, inject the standard mixture several times until successive runs give results within the repeatability of the method (see 8.2).

7.2.2.3 Always inject the same volume of standard and sample. If the difference in concentrations of a component in the standard and sample is greater than a factor of × 2, select a more appropriate standard mixture.

NOTE 9 Because of the nature of the detector response, changes in injection bandwidth, such as would be caused by different sample sizes, can have an effect upon peak shape which could cause large errors. For the same reason, it is not advisable to use a standard consisting of a liquid mixture when analysing gas samples.

7.3 Test

Inject, using a syringe or a bypass injector, a portion of the sample to be analysed. Inject the same volume of appropriate standard mixture under the same conditions (see 7.2.2.3). Select the sample size so that the sulfur content falls within the range 0,5 ng to 50 ng. For example, a 0,5 ml sample containing 1 µmol/mol of a sulfur compound (1 S atom/molecule) will contain 0,7 ng of sulfur. Larger contents of sulfur in the sample will saturate the detector response.

7.4 Examination of the chromatogram

7.4.1 Figure 1 shows a chromatogram of natural gas containing a mixture of odorants (ethanethiol, 2-methyl-2-propanethiol, methyl ethyl sulfide and diethyl sulfide).

Figure 2 shows a chromatogram of natural gas containing a high level (2 000 µmol/mol) of hydrogen sulfide and a range of thiols.

7.4.2 The following relative retention times were found when following the procedure described in 7.1 to 7.3. They can be expected to vary somewhat depending on the instruments used and should be confirmed by the user.

Component	Relative retention time
Methane	0,04
Ethane	0,16
Hydrogen sulfide	0,25
Carbonyl sulfide	0,40
Propane	0,62
Methanethiol	1,00
i-Butane	1,08
n-Butane	1,19
Ethanethiol	1,46
Dimethyl sulfide	1,49
2-Propanethiol	1,78
1-Propanethiol	1,90
Methyl ethyl sulfide	1,90
2-Methyl-2-propanethiol	2,01
2-Methyl-1-propanethiol	2,19
Diethyl sulfide	2,24
1-Butanethiol	2,29
Tetrahydrothiophene	2,46

The identification of sulfur compounds can be assisted by selective removal. Washing a gas sample with sodium hydroxide solution removes hydrogen sulfide and thiols. Washing with silver nitrate solution also removes sulfides. This can be done by adding a few millilitres of a molar aqueous solution of the reagents to a glass bulb containing the gas, and shaking it to ensure good contact, or by passing the gas through glass tubes in which the solution is impregnated onto an inert support, such as celite1).

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1) Celite is an example of a suitable product available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

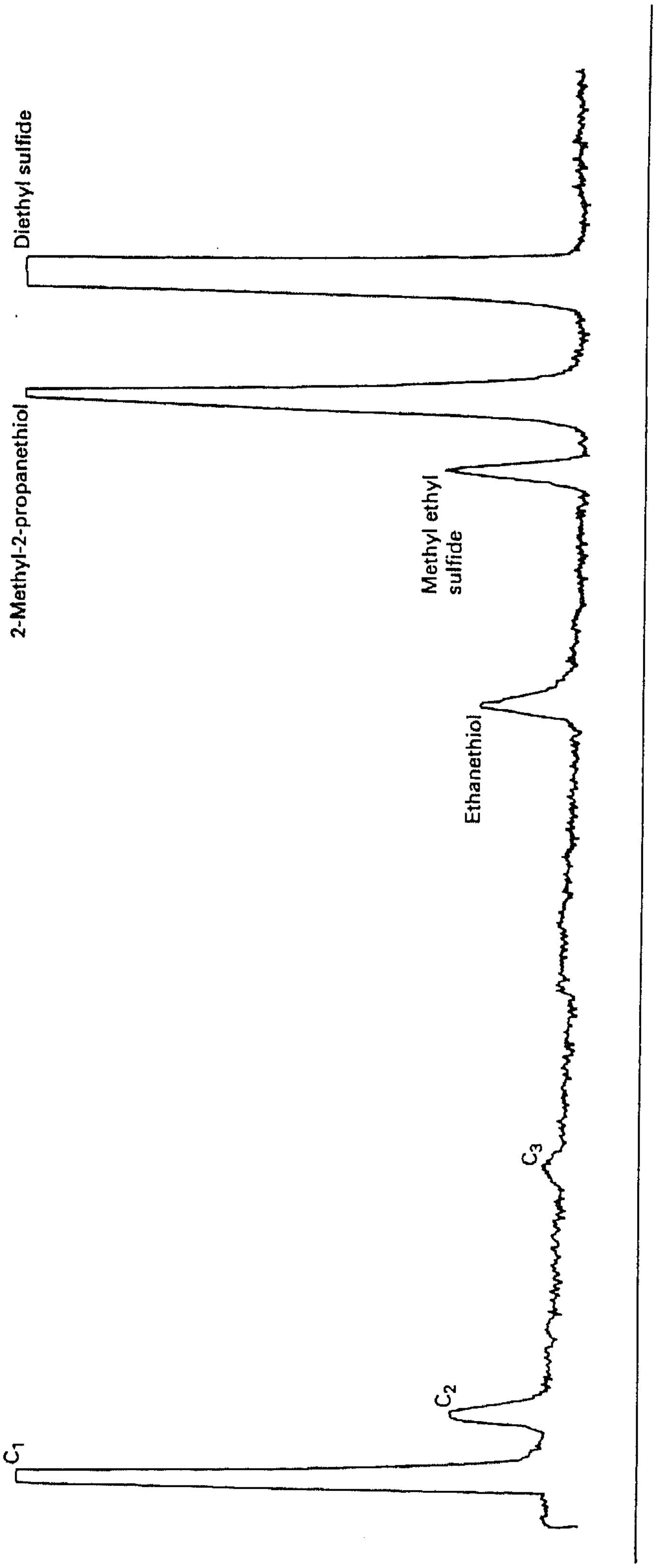

Figure 1 — Chromatogram of natural gas containing a mixture of odorants

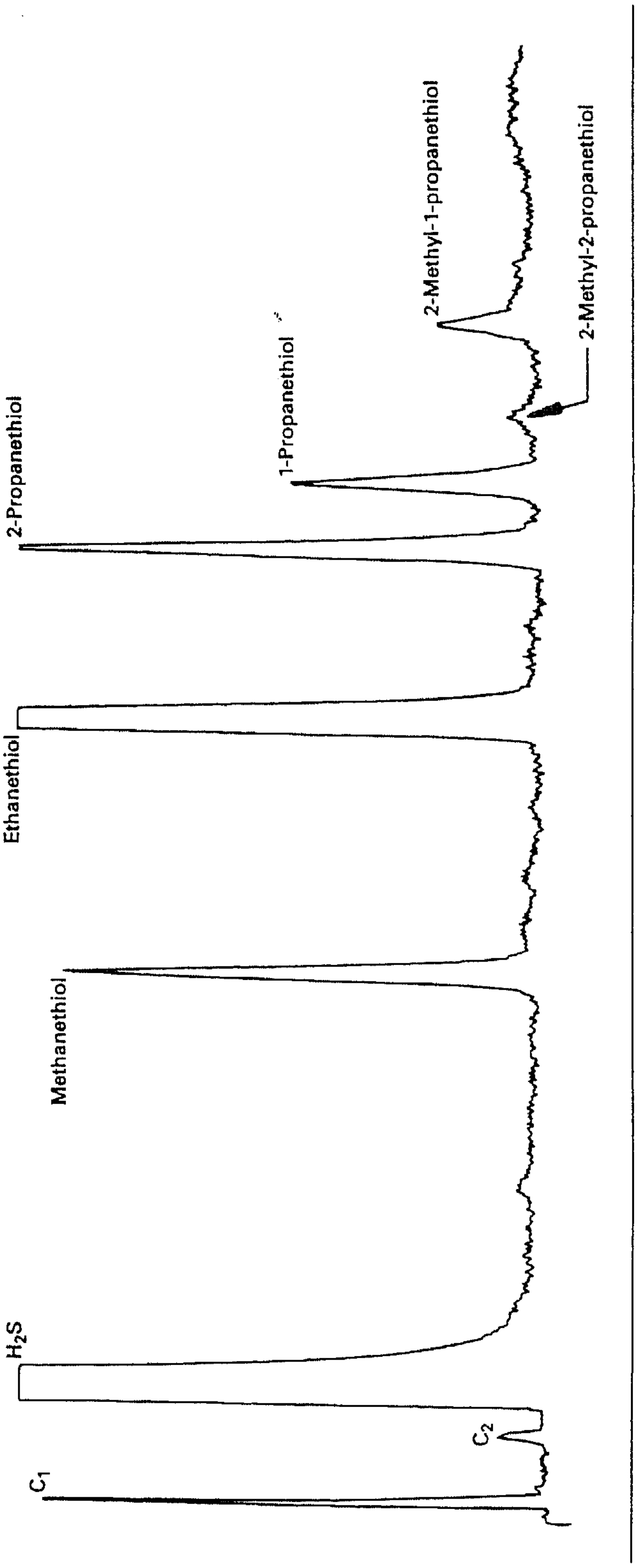

Figure 2 — Chromatogram of natural gas containing a high level of hydrogen sulfide and a range of thiols

8 Expression of results

Component concentrations shall be expressed in micromoles per mole. Concentrations below 10 µmol/mol shall be expressed within 0,1 µmol/mol and higher concentrations within 1 µmol/mol.

8.1 Calculation

Measure the signal of the component peaks in both the sample and the standard. Where a component has been measured at different attenuations in the sample and standard, convert the measurement to the same attenuation.

Calculate the concentration (x_i) of each component (i) in the sample according to the formula

$$x_i = E_i \times \left(\frac{H_i}{H_E} \right) \times \frac{1}{n}$$

where

E_i is the concentration of component i in the standard mixture;

H_i is the signal due to component i from the chromatogram of the sample;

H_E is the signal due to component i from the chromatogram of the standard mixture;

n is the exponent measured for the relationship:

$$A = k \times c^n$$

where

A is the signal H_i or H_E;

k is a constant;

c is the concentration x_i or E_i.

The signal H_i or H_E, may be measured as a peak height or peak area. In both cases, a consistent approach shall be used for both the sample and the standard, and a component in the sample can only be compared with the same component in the standard.

For the most accurate results, several standard gases containing component levels covering the range of interest shall be analysed, and the value of the exponent (n) redefined. This value can then be used to plot a calibration curve, or fitted into the data handling algorithm.

8.2 Precision

The repeatability of the method, as a relative value, is about 10 % for all components.

The reproducibility of the method has not been established.

9 Test report

The test report shal contain at least the following information:

a) a reference to this part of ISO 6326;

b) all information necessary for complete identification of the sample, for example:

- the date and time of sampling into the cylinder;
- the place in the pipeline system at which the sample was taken;
- the conditions of the gas in the pipeline system, such as temperature, pressure and throughput;

c) the sampling method used (including the size and type of material and the temperature of the high pressure cylinder);

d) any deviation from the procedure specified;

e) a complete list of all components determined or detected;

f) the concentrations of all components determined;

g) if possible, the precision of the determined concentrations of the components in the sample, including the number of determinations;

h) any unusual features noted during the determination (i.e. in the chromatogram).