
International Standard



6326/2

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**Gas analysis — Determination of sulphur compounds in natural gas —
Part 2 : Gas chromatographic method using an electrochemical detector for the determination of odoriferous sulphur compounds**

Analyse des gaz — Détermination des composés soufrés dans le gaz naturel — Partie 2 : Méthode par chromatographie en phase gazeuse avec détecteur électrochimique pour la détermination des composés soufrés odorants

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up 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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 6326/2 was developed by Technical Committee ISO/TC 158, *Analysis of gases*, and was circulated to the member bodies in September 1979.

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It has been approved by the member bodies of the following countries:

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Belgium	Germany, F. R.	Poland
Bulgaria	Korea, Rep. of	Romania
Czechoslovakia	Libyan Arab Jamahiriya	South Africa, Rep. of
Egypt, Arab Rep. of	Netherlands	USSR
France	Philippines	

The member bodies of the following countries expressed disapproval of the document on technical grounds:

India
United Kingdom

Gas analysis — Determination of sulphur compounds in natural gas —

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

0 Introduction

The standardization of several methods for the determination of sulphur compounds in natural gas is necessary in view of the diversity of these compounds (hydrogen sulphide, carbonyl sulphide, thiacyclopentane, 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, this International Standard has been prepared in several parts.

Part 1¹⁾ gives a rapid comparison of standardized methods and therefore provides information for the choice of the method.

The other parts, including part 2, describe in detail the various standardized methods.

The determination of total sulphur is specified in ISO 4260, *Petroleum products — Determination of sulphur content — Wickbold combustion method.*²⁾

1 Scope and field of application

This part of ISO 6326 specifies a gas chromatographic method for the qualitative and quantitative analysis of odoriferous sulphur compounds in natural gas.

Sulphur compounds may occur naturally in natural gas and remain as traces after treatment, or they may have been injected deliberately to allow subsequent olfactory detection.

The method is applicable to the following compounds :

- hydrogen sulphide;
- methanethiol³⁾ and homologues up to butanethiols;
- thiacyclopentane⁴⁾.

It is not applicable for the determination of carbonyl sulphide.

Under normal conditions of application, this method can be used to determine the content of each compound within a concentration range from 0,1 to 100 mg (concentration expressed in milligrams of sulphur) per cubic metre of gas at standard pressure and temperature.

The detector used is not sensitive to the major components of natural gases.

NOTES

The chromatographic conditions described enable hydrogen sulphide and methanethiol to be determined if the ratio of the concentration of the former to the concentration of the latter is less than 10. The same applies for two thiols eluted consecutively. The resolution of the chromatographic column can be improved to increase this ratio.

2- The method can also be used to determine the contents of

— the same sulphur compounds in air. If such an application is contemplated, it is appropriate, however, to take account of possible interferences from gases or vapours which can be detected by the electrochemical cell, and which could contaminate the atmosphere under consideration;

— organic sulphides and disulphides; the conditions of analysis are however different and are not within the scope of this International Standard.

3 See the bibliography concerning the method described in this International Standard.

2 Apparatus

The apparatus operates at room temperature (see 3.4.2) and consists essentially of four parts.

2.1 Device for sample injection

To avoid adsorption and desorption phenomena, the use of metal in this part of the apparatus shall be restricted.

1) In preparation.

2) At present at the stage of draft.

3) Trivial name : methyl mercaptan.

4) Trivial name : tetrahydrothiophene (THT). For the determination of the content of this compound only, see the annex.

2.1.1 Manual injection

The sample is taken using a gas syringe, and immediately injected through a PTFE septum at the top of the column.

2.1.2 Automatic injection

A programmer controls the injection line valves for the gas to be analysed. The non-metallic parts of the injector are of polyamide (loops) or PTFE (seats of electromagnetic valves).

2.2 Column

2.2.1 Tube

Material : glass
Internal diameter : 4 mm
Length : 40 cm

2.2.2 Packing

2.2.2.1 Support

Nature : Chromosorb W
Particle size : 150 to 180 µm (80 to 100 mesh, Tyler series)

2.2.2.2 Stationary phase

For the first two-thirds of the column length : silicone DC 200, 40 g per 100 g of support.

For the last third : dinonyl phthalate, 40 g per 100 g of support.

2.3 Electrochemical detector (see the figure)

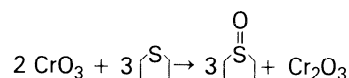
This consists of a glass or methyl polymethacrylate container. The electrodes, two pieces of platinum gauze (diameter 35 mm, 3 600 wires per cm²), are welded 30 mm apart in a borosilicate glass tube and separately connected to the amplifier or to the recorder by a platinum wire.

The electrolyte, a 10 % solution of chromic oxide in distilled water, is contained in a vessel into which the tube with the electrodes dips such that the solution is retained by capillarity within the tube at the level of the upper grid, the level in the vessel itself being approximately mid-way between the two grids.

The gas flow from the chromatographic column is discharged through a glass tube of 2 mm internal diameter, 5 mm above the upper grid centre.

As soon as elution of a sulphur compound occurs, a redox-reaction occurs on the surface electrode creating a potential difference between the two electrodes, thus causing a current which is observed in a low resistance measuring circuit. For

example, thiacyclopentane is oxidized to tetramethylene sulphoxide according to the reaction



2.4 Recorder

Type : potentiometric
Sensitivity : 1 mV full scale
Response time : of the order of 1 s

NOTE — If the detector is fitted with an amplifier, a 1 V full scale recorder may be used.

It is possible to use various data retrieval and processing devices :

- integrator and printer;
- integrating calculator and printer;
- integrator and programmable calculator.

The advantage of the last two devices is that they allow both the identification and determination of sulphur compounds contents.

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3 Procedure

3.1 Preparation of the apparatus

3.1.1 Carrier gas

Nature : nitrogen
Pressure : approximately 2 bar
Flow rate : 100 ml/min at 20 °C

3.1.2 Check for absence of leaks

3.1.3 Check of the electrolyte level

3.1.4 Adjustment of the recorder zero setting

3.1.5 Automatic injection

Adjust the flow rates of the gas to be analysed and the calibration gas mixture to 150 ml/min to purge the injection loop.

3.2 Analysis

Inject 20 ml of the sample, irrespective of the injection device used.

This is the maximum volume and can be reduced when the concentration of sulphur compounds is high. If the operation is automatic, the duration of the analysis cycle, including the injection and elution stages, is 1 h.

3.3 Examination of the chromatogram

3.3.1 Qualitative analysis

The order and elution time for various constituents at 20 °C for a flow rate of 100 ml/min is :

hydrogen sulphide (for manual operation only)	30 s
methanethiol	60 s
ethanethiol	80 s
propane-2-thiol	160 s
2-methylpropane-2-thiol	240 s
propane-1-thiol	290 s
butane-2-thiol	560 s
thiacyclopentane	2 100 s

Duration of analysis : 45 min

NOTE — In order to reduce the total time of the analysis, the column described in the annex, for the determination of thiacyclopentane, may be used in parallel with the column described in 2.2.

The elution of thiacyclopentane may also be accelerated either by increasing the flow rate of the carrier gas, after the elution of butane-2-thiol, from 100 to 500 ml/min by means of an automatic device, or by using only approximately the first third of the column described in 2.2 for the elution of thiacyclopentane, by means of a commutation valve placed on the column at this distance. In these last two cases, the total time of analysis is only 15 min whilst still using only a single injection.

3.3.2 Quantitative analysis

3.3.2.1 Calibration

Carry out external calibration.

Because the physical and chemical characteristics of the compounds analysed are very different, several types of calibration mixture have to be considered.

- Calibration gas mixtures prepared by a variant of the manometric method.¹⁾ It is easy to prepare a mixture for calibration under pressure where the component is thiacyclopentane and the complementary gas is nitrogen. Such a mixture is stable when stored in a light alloy cylinder.
- Calibration gas mixtures prepared by the permeation method²⁾ on a gas flowing at a known rate. This is the technique recommended for preparing mixtures of components such as hydrogen sulphide and methanethiol.
- Liquid calibration mixtures. This is the case with ethanethiol, its higher homologues and thiacyclopentane. Mixtures of such products in cyclohexane are stable. They should, however, be kept in a refrigerator if they are to be used over a long period.
- Calibration mixtures for deferred injection. Under automatic conditions using an integrating calculator, it is

useful to inject a calibration mixture containing only one component at a point in the cycle such that the elution of the latter occurs clear of the components of the gas being analysed. Knowledge of the relative response factors with respect to this compound enables the concentration of the sulphur compounds to be determined in the gas being analysed. The component of this calibration mixture prepared by the manometric method may be one of the compounds to be analysed (thiacyclopentane) or a different substance (methyl ethyl sulphide).

3.3.2.2 Calculation of concentration

Use the following formula

$$x_i = E_i \frac{A_i}{A_E}$$

where

x_i is the content of substance i in the sample;

E_i is the content of compound i in the calibration mixture;

A_i is the measurement of peak i on the sample chromatogram;

A_E is the measurement of peak i on the chromatogram for the calibration mixture.

3.4 Precautions to be taken to obtain satisfactory quantitative results

3.4.1 Sampling

To minimize adsorption phenomena in the transfer line, the following conditions shall be observed :

- The gas to be analysed shall be taken from a stream directly connected to the main stream. Taking a sample from a dead space would give erroneous results.
- The only materials that can be used for the transfer line are PTFE and polyamide. However, in the case of high gas flow rates, stainless steel can be used. Copper and its alloys are specifically to be avoided as well as pressure reducing valves containing rubber parts.
- Analysis is representative only if the gas is taken from a pipe in which the gas flow is sufficiently high.
- When gases having different sulphur compounds contents are analysed consecutively, care shall be taken that the line is purged until stable conditions are achieved.

1) See ISO 6146, *Gas analysis — Preparation of calibration gas mixtures — Manometric method*.

2) See ISO 6349, *Gas analysis — Preparation of calibration gas mixtures — Permeation method*.

3.4.2 Detector

The detector is sensitive to sudden temperature changes. It shall therefore be placed in surroundings with a constant temperature, or, better, in a temperature-controlled environment.

The relationship between detector response and concentration is not strictly linear. A calibration mixture shall, therefore, be used in which the concentration of each component is close to the concentration of the same component in the natural gas to be analysed. This obviously limits the application of automatic methods for gases with large variations in composition.

3.5 Handling precautions

All sulphur compounds present a fairly high toxic hazard. Their odour, even at low concentration levels, is extremely disagreeable. All safety precautions concerning sample handling and gas mixture preparation shall, therefore, be observed. Care shall also be taken that the lines are gas-tight.

4 Accuracy

The repeatability of the method is better than 5 %.

The method enables the concentration of each compound to be determined with an accuracy of about 10 %.

5 Test report

The test report shall contain the following information :

- a) Sampling conditions :
 - pressure;
 - temperature;
 - date.
- b) Results of the analysis :
 - the concentrations, expressed in milligrams of sulphur per cubic metre of gas (under standard conditions of pressure and temperature).

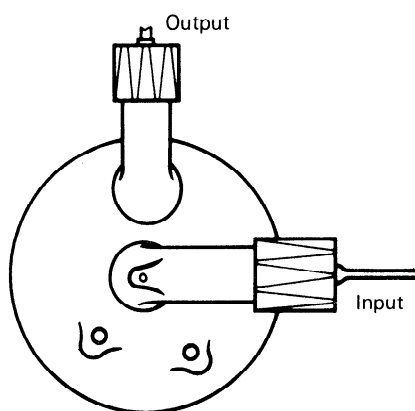
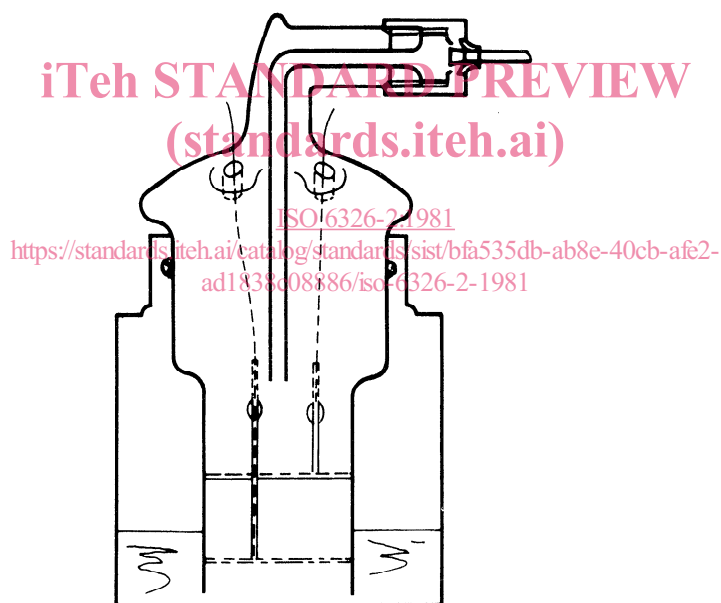


Figure — Electrochemical detector

Annex

Determination of thiacyclopentane only

If only thiacyclopentane is to be determined, it is advisable to decrease its retention time to about 300 s to increase the speed of analysis.

For occasional determinations, the flow rate of the carrier gas may be increased (500 ml/min).

For continuous determinations, it is preferable to use a different packing. Use a 40 cm column filled with the same silicone-impregnated support, DC 200, in the ratio 20 g per 100 g of support.

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