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Natural gas — Determination of sulfur compounds using gas chromatography

Gaz naturel — Détermination des composés soufrés par chromatographie en phase gazeuse

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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 19739 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*.

This first edition of ISO 19739 cancels and replaces ISO 6326-2:1981 and ISO 6326-4:1994, of which it constitutes a technical revision.

Introduction

Sulfur 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 for safety reasons.

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, tetrahydrothiophene, etc.) and the requirements of the determinations (e.g. required uncertainty, measurement at the drilling head, clean-up plant or in transmission pipes).

In order to enable its user to choose the most appropriate method for his/her particular needs and perform the measurements under the best conditions, this International Standard gives the requirements needed to perform a sulfur analysis.

Natural gas — Determination of sulfur compounds using gas chromatography

WARNING — Some sulfur compounds can constitute a serious health hazard.

1 Scope

This International Standard specifies the determination of hydrogen sulfide, carbonyl sulfide, C_1 to C_4 thiols, sulfides and tetrahydrothiophene (THT) using gas chromatography (GC). Depending on the method chosen from those given in the annexes, the application ranges for the determination of sulfur compounds can vary, but whichever of the methods is used, the requirements of this International Standard apply.

2 Normative references

The following referenced documents are indispensable for the application 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 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

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

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

ISO 6145-10, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 10: Permeation method*

ISO 10715:1997, *Natural gas — Sampling guidelines*

ISO 14532:2001, *Natural gas — Vocabulary*

3 Terms and definitions

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

3.1
alkane thiol
alkyl mercaptan
organic sulfur compound with the general formula R-SH (where R is the alkyl group), either naturally present or added as an odorant to natural gas

[ISO 14532:2001, definition 2.5.3.3.1]

EXAMPLE Methanethiol (MeSH), ethanethiol (EtSH), 2-methylpropane-2-thiol (tert-butylmercaptan TBM).

3.2
alkyl disulfide
organic sulfur compound with the general formula R-S-S-R (where R and R are alkyl groups)

[ISO 14532:2001, definition 3.5.3.3.3]

3.3
alkyl sulfide
thioether
organic sulfur compound with the general formula R-S-R (where R and R are alkyl groups), either naturally present or added as an odorant to natural gas

[ISO 14532:2001, definition 3.5.3.3.2]

EXAMPLE Dimethyl sulfide (DMS), diethyl sulfide (DES).

3.4
carbonyl sulfide
COS
sulfur compound found in natural gas, which contributes to the total sulfur content

[ISO 14532:2001, definition 3.5.3.3.4]

3.5
chromatographic resolution
column efficiency characteristic describing the degree of separation of two adjacent peaks in gas chromatography

[ISO 14532:2001, definition 2.5.3.4.6]

NOTE The resolution is measured as twice the distance between the maximum of the named peaks divided by the sum of the intercepts on the baseline made by tangents drawn to the peaks at half the height.

3.6
cyclic sulfide
thioether
cyclic organic sulfur compound with one sulfur atom incorporated in a saturated hydrocarbon ring

EXAMPLE Tetrahydrothiophene (thiophane or thiacyclopentane, THT), i.e. C_4H_8S, which is added as an odorant to natural gas.

[ISO 14532:2001, definition 2.5.3.3.6]

3.7
hydrogen sulfide
H_2S
colourless, toxic gas with an odour similar to rotten eggs

[ISO 14532:2001, definition 2.5.3.3.8]

3.8
normal reference conditions
reference conditions of pressure, temperature and humidity (state of saturation) equal to 101,325 kPa and 273,15 K for a dry, real gas

[ISO 14532:2001, definition 2.6.1.3]

3.9
standard reference conditions
reference conditions of pressure, temperature and humidity (state of saturation) equal to 101,325 kPa and 288,15 K for a dry, real gas

[ISO 14532:2001, definition 2.6.1.4]

3.10
total sulfur
total amount of sulfur found in natural gas

[ISO 14532:2001, definition 2.5.3.3.17]

NOTE The total amount of sulfur may be determined by an analytical method not differentiating between individual sulfur compounds.

3.11
working reference gas mixture
WRM
working standard gas mixture
gas mixture whose component quantity levels have been validated by direct comparison with a secondary standard gas mixture (CRM)

[ISO 14532:2001, definition 2.5.3.5.2.3]

3.12
secondary standard gas mixture
gas mixture whose component quantity levels have been validated by direct comparison with a PSM

[ISO 14532:2001, definition 2.5.3.5.2.2]

3.13
primary standard gas mixture
PSM
gas mixture whose component quantity levels have been determined with the utmost accuracy and can be used as a reference gas for determining the component quantity levels of other gas mixtures

[ISO 14532:2001, definition 2.5.3.5.2.1]

4 Principle

All significant components or groups of components to be determined in a gaseous sample are physically separated by means of gas chromatography (GC) and measured by comparison with calibration or reference gases. The gas being used for calibration and the sample gas shall be analysed with the same measuring system under the same set of conditions

5 Apparatus

5.1 Gas chromatograph, containing injection device, oven, regulation system for temperature control and pressure, detector.

5.2 Chromatographic columns, with column tubing made of a material inert to sulfur compounds (see 6.4), and a stationary phase able to separate the sulfur compounds to be analysed in order that the resolution between two adjacent peaks shall not be less than 1,5.

NOTE 1 See Annex A for a list of chromatographic columns mostly used in sulfur analysis.

NOTE 2 The absence of chromatographic separation between COS and H_2S will lead to an error in total sulfur amount calculation.

5.3 Detectors for detecting sulfur compounds:

— sulfur-specific,

— multi-specific (respond to halogen, sulfur), and/or

— general detectors.

See Annex B for descriptions of suitable detectors.

NOTE 1 Separation problems on a column could be solved by using a sulfur-specific detector, as hydrocarbons will not be seen by it.

NOTE 2 Matrix effects can occur in sulfur analysis with certain methods/detectors.

NOTE 3 Sulfur response can be affected by quenching effects produced by hydrocarbons.

NOTE 4 Many detectors use an excited state of a molecule or atom to detect sulfur. An atom or molecule with one electron shifted from its normal orbit to another (more energetic) is said to be excited. When it relaxes, returning to its normal state, the electron falls back to its normal orbit emitting a photon. The energy of this photon is relative to the difference in energy between the orbits. The wavelength of the photon is specific for each excited state. So, if photons of different wavelength are separated (by a filter, monochromator, diffraction prism, etc.), the amount of specific photons can be measured.

6 Sampling

The sampling procedures are very important in the analysis of sulfur compounds. Sulfur compounds have a strong tendency to adsorb on to, or to chemically react with, different materials of construction. Low contents of sulfur compounds in samples and calibration gas mixtures place demands on the sampling procedure to ensure that the sulfur compounds in correct quantity reach the analytical detector.

Carry out representative sampling in such a way that the sample represents the bulk of the gas at the time of sampling. Sampling and sample transfer shall be in accordance with ISO 10715.

Purge time should be long enough to have replicate stable analytical results within the acceptable standard deviation of the analyser. Purge time needed will depend on the type and concentration of the sulfur compound, materials of construction in gas contact and the gas flow through the sample loop.

6.1 Safety precautions

Safety precautions required in handling gas cylinders with pressurised flammable gas mixtures are described in the ISO 10715. If a pressure regulator is to be connected to the cylinder, always use a regulator with materials of construction recommended by the producer of the calibration gas.

6.2 Temperature control

When a cylinder of a calibration or sample gas mixture arrives at the place of use, ensure that the cylinder temperature is kept above the condensation temperature (as stated on the certificate). If condensation may have occurred during transportation or storage, store the cylinder at ambient temperature in a horizontal position for at least 7 days. Rolling of the cylinder will lower the homogenisation time.

Always store both calibration and sample gases at the same suitable temperature.

To reduce any adsorption of low concentration levels of sulfur compounds when using the calibration gas or a sample, the transfer lines from the cylinder and the bypass injection valve should be heated (to, for example, 90 °C).

6.3 Construction materials

The presence of sulfur compounds in the calibration or sample gas makes the choice of materials of construction in the pressure reduction device, the transfer line, the sample loop and the separation column very important. The general considerations of ISO 10715 should always be followed.

6.4 Cleanness

When a calibration or sample gas cylinder is to be connected to a gas system, always inspect visually the connection on the cylinder valve outlet. Carefully clean out any dirt, dust or particles with a dust-free cloth. Any trace of humidity is to be purged out with dry inert gas.

Make sure that all transfer lines are free of dirt, rust, grease or other particles. Change all tubing/fittings if there is any suspicion of impurities. Particle filters may be helpful, but they shall only contain material proposed in ISO 10715.

6.5 Installation of the calibration gas cylinder

The installation of a calibration gas cylinder and use of the certified gas mixture is dependent on the method by which a gas sample is taken and is to be analysed/compared. To minimise the surface in gas contact, it is important to connect the calibration gas as near as possible to the injection point. One principle for the connection of a calibration gas cylinder in direct sampling is shown in ISO 10715:1997, Annex A.

6.6 Pressure control

As described for the sample handling in ISO 10715, very often a pressure reduction device is required in order to feed the calibration and sample gas to an analyser. Normally, this is a reduction valve connected directly or close to the calibration and sample gas cylinder. Only use a pressure regulator made of the material approved by the producer of the calibration gas mixture.

To further minimise any adsorption effects, a fine regulating needle valve (made in approved material) could be connected directly to the cylinder valve. Be sure that the certified pressure range of this valve suits that of the total system and that no local or national safety regulation prohibits such an arrangement.

Never use a calibration gas mixture with a total pressure lower than that recommended on the certificate. If no recommendation is stated, stop using the mixture if the total pressure is lower than 10 % of the certified filling pressure.

Always use the same reduced pressure when injecting the calibration mixture and the natural gas sample. Control the purge flow by a needle valve, not by adjusting the reduction pressure valve.

If several calibration gases with different concentrations of the sulfur compounds are used, it is very important to always use the same needle valve for the same calibration gas mixture. Be aware of the need to change needle valves to different concentration levels.

6.7 Purging of reduction valve and transfer lines

Due to the strong tendency of sulfur compounds to adsorb to different materials of construction, it is important to purge all surfaces (which are in contact with the gas) from the cylinder valve to the injection point. Using a pressure-reducing valve mounted directly onto the cylinder valve connection, the purging should include a number of “fill and empty” cycles as described in ISO 10715. A good practice is also to connect the total transfer line from the reducing valve to vent and include the purge all the way through the sample loop.

When analysing calibration gases with different concentration levels, always flush the transfer lines and the valves with dry N_2 in order to avoid memory effects.

6.8 Flow control

As stated in ISO 10715, turbulent flow is advantageous in a sampling system. The flow rate of the calibration gas with 3,175 mm (1/8 in) tubing should at least be 80 to 100 ml/min. When purging a calibration gas for analytical comparison with natural gas samples, the flow rate should be the same as the sample gas flow rate.

With light gases like H_2 or He in the calibration gas mixture, it may be of importance that the purge flow rate of calibration gas mixtures is never below 10 ml/min, in order to avoid separation effects of lighter versus heavier gases (effusion).

Stopping of flow just before injection of the standard/sample is the best way to minimize differences in the injected gas volumes due to back-pressure variations. However, be aware of any change in atmospheric pressure during the total analysis.

6.9 Diffusion control

Any leakage caused by diffusion of air-in or gas mixture out should be avoided by using pressure regulators with non-permeable membranes.

Be aware that using polymer types of tubing in gas transfer lines may cause problems related to diffusion of humidity from the environmental air.

6.10 Automation and sequences of sampling

With repeated injections and in order to get stable response from each sulfur compound in calibration and sample gas mixtures, a programmable automatic gas sampling valve should be installed and used. Normally, the tendency is that, due to adsorption phenomena, the peak from some sulfur compounds increases during the first injections, but after a few repeated injections the peak areas become more and more stable. The number of repeated injections required is to be defined based on achieved areas from each sulfur compound.

Repeated injections of the same calibration mixture before and after comparison analysis with one or more samples gives a good indication of any drift in the detector response during the total analytical time.

7 Calibration

Perform regular calibration using working standard gas mixtures certified in accordance with ISO 6143 or permeation devices according to ISO 6145-10. The working standard gas mixtures shall contain appropriate number and concentrations of sulfur compounds in methane or natural gas depending upon the detector characteristics (e.g. hydrocarbon quenching). A certificate of mixture according to ISO 6141 should always be available with the cylinder.

NOTE 1 Sulfur compounds at low concentrations in gas mixtures are easily lost by sorption or reaction. The preparation of such mixtures requires that extreme care be taken with the cleanliness of the surfaces of cylinders and of tubing used for transfer, with the purities of the components used, particularly the matrix gas, and with the preparation procedure. Stability of the mixture can be demonstrated by regular repeat analyses of the contents, using as reference a dynamically prepared mixture of similar composition. A demonstrated history of preparation of mixtures which have been successfully assessed for stability is the best form of assurance for the user.

NOTE 2 Another problem with diffusion is caused by connecting reduction valves to the cylinders. The air contained in the reduction valve will diffuse into the cylinder when the cylinder value is opened while the reduction valve is still closed. The oxygen will, for example, oxidize mercaptans to disulfides.

8 Analysis

Perform quantitative analysis and determine the mass concentration and uncertainty budget of the different sulfur compounds in natural gas in accordance with ISO 6143.

Be aware of the special adsorption and/or chemical problems that can occur with the handling of sulfur gas components. Repeated injections of the same working reference gas mixture before and after comparison analysis may give an indication of any drift due to sulfur adsorption during the total analytical time.

9 Performance characteristics required for sulfur analysis

The performance characteristics required for sulfur analysis were determined from a proficiency test performed by seven laboratories in different countries. The following two mixtures — given here with their compound/IUPAC name and mass concentration expressed in milligrams per cubic metre (under normal reference conditions) — were analysed.

a) Mixture 1

- Hydrogen sulfide (H_2S): 3 mg/m^3
- Methane (CH_4): matrix

b) Mixture 2

- Carbonyl sulfide (COS): 5 mg/m^3
- Methanethiol (MeSH): 5 mg/m^3
- Ethanethiol (EtSH): 5 mg/m^3
- 2-Methylpropane-thiol (TBM): 6 mg/m^3
- Diethyl sulfide (DES): 10 mg/m^3
- Tetrahydrothiophene (THT): 25 mg/m^3
- Methane (CH_4): matrix

The seven laboratories used different methods and calibration gases. The data obtained are given in Table 1.

Table 1 — Performance characteristics for sulfur analysis

Compound	Mass concentration (sulfur compound in methane) mg/m^3 (norm. ref. cond.)	Achievable repeatability (absolute) mg/m^3 (norm. ref. cond.)	Achievable repeatability (relative) %	Proficiency agreement (relative) %
H_2S	3	0,1	3	25
COS	5	0,1	2	15
MeSH	5	0,1	2	10
EtSH	5	0,2	4	30
TBM	6	0,4	7	25
DES	10	0,2	2	20
THT	25	1,0	4	20

Proficiency agreement values quoted in Table 1 were calculated based on z-scores as defined in Reference [5] (see 4.1, 4.2, 4.3), and are the limits between which two laboratories shall be able to achieve a result of analyzing a known standard using different methods and calibration gases. The two laboratories analyze a standard of known mass concentration of 25 mg/m^3 of THT. If their results lie within the range of 19 mg/m^3 and 31 mg/m^3, then they are comparable, i.e. 25 mg/m^3 $\pm$ 5 mg/m^3 (20 % of the proficiency agreement given in Table 1) $\pm$ 1 mg/m^3 (4 % of the achievable repeatability given in Table 1).

The repeatability shown in Table 1 was calculated in the following way: two times the standard deviation based on $n-1$ values (95 % confidence interval, see ISO 5725-2), free of outliers (see ISO 5725-2:1994, 7.3.4.1), assuming a normal distribution calculated with 5 analyses.

10 Test report

The test report shall include at least the following information:

a) reference to this International Standard and the analytical method used;

b) sample identification including

- time/date of the sampling,
- sample point/stream (location), and
- cylinder identification (for spot sampling);

c) reference to the calibration system used;

d) sample mass concentration, including the number of digits appropriate to the certificate of WRM and size of error, including the result of uncertainty calculation;

e) comments, including

- any deviation from specified procedure, and/or
- problems concerning the sample;

f) date of analysis, name of laboratory and signature of analyst.

Annex A
(informative)

Columns mostly used in sulfur analysis (with internal phase and dimensions)

Stationary phase	Dimensions	Type	Film thickness of stationary phase *df* μm	Compounds
100 % dimethylpolysiloxane	50 m × 0,32 mm	Capillary	5	Hydrogen sulfide, mercaptans, carbonyl sulfide, diethyl sulfide, dipropyl sulfide
100 % dimethylpolysiloxane	30 m × 0,32 mm	Capillary	4	Hydrogen sulfide, carbon disulfide, sulfur dioxide
Porous layer open tubular	30m × 0,32 mm	Capillary	4	Hydrogen sulfide, carbonyl sulfide, mercaptans
Styrene-divinylbenzene polymer	30 m × 0,32 mm	Capillary	10	Hydrogen sulfide, carbonyl sulfide, methyl sulfide, mercaptans, tetrahydrothiophene
5 % phenyl-95 % dimethylpolysiloxane	25 m × 0,53 mm	Capillary	5	Hydrogen sulfide, mercaptans, carbon disulfide, carbonyl sulfide, dimethyl disulfide, dimethyl sulfide, sulfur dioxide, thiophene
50 % phenyl 50 % dimethylpolysiloxane	1,5 m × 3,175 mm (1/8 in)	Packed	80 to 100 mesh	Hydrogen sulfide, carbonyl sulfide, mercaptans
100 % dimethylpolysiloxane	1,5 m × 3,175 mm (1/8 in)	Packed	80 to 100 mesh	Hydrogen sulfide, carbonyl sulfide
40 % dynonyl phthalate	30 cm	—	80 to 100 mesh	Tetrahydrothiophene, mercaptans
NOTE This is not an exhaustive list. Recent developments could lead to other columns being available.				

Annex B
(informative)

Types of detectors used in sulfur analysis

B.1 General

For a summary of the characteristics of the types of detectors described here, see Table B.1.

B.2 Atomic emission detector (AED)

The effluents of the gas chromatograph come into a cavity where a plasma is induced and sustained by different energy forms (mostly by microwave induction). The photons emitted by the relaxing atoms may then be separated by wavelength and measured. This detector is specific for different atoms.

See Annex F.

B.3 Electrochemical detector (ED)

The effluents of the gas chromatograph are gently blown on the surface of an electrolyte where sulfur compounds react. This reaction induces an electron flow (redox reaction). Two electrodes dip into the electrolyte to measure this induced current. This detector is multi-specific for different compounds, depending on the chosen electrolyte.

See Annex D.

B.4 Electron capture detector (ECD)

The electron capture detector contains a radioactive source used to create an electron flow. This flow is measured by electrodes. When the effluents of the gas chromatograph pass through this cell, some electrons might react with the effluents, thus changing the measured current (DC voltage mode). The specificity depends on the differences of compound affinity for electrons. Response is then strongly compound-dependent.

B.5 Flame photometric detector (FPD)

The effluents of the gas chromatograph are burnt into an FID type flame with specific H_2/air ratios. When so burned, sulfur and phosphorus containing hydrocarbons will produce fluorescent species (which can be compared to an excited molecule). During the relaxation of these species, specific photons will be emitted. These are separated by an optical filter and can then be measured. Many variations exist (single-flame, dual-flame, linearized response, pulsed). This detector is specific. There are known interferences (quenching) with hydrocarbons, the response is non-linear but often can be electronically corrected. New developments of this detector are made to limit these problems.

See Annexes C and G.

B.6 Pulsed flame photometric detector (PFPD)

Like the FPD, this detector uses a flame, but it can provide better sensitivity and selectivity for sulfur and phosphorus. Two different combustible gas flows enter the bottom of the combustion chamber through narrow gas lines (the FPD, in contrast, has only one). The second incoming gas flow's job is to help fill up the outer volume of the combustion chamber while the analyte and the primary combustion gas flow into that chamber. This second flow also helps to optimize the analyte emission brightness in the combustion process. At the top of the PFPD is an ignition wire which stays continuously red-hot. Then the gases flowing into the combustor including the analytes exiting the GC column reach a flammable mixture they are ignited by the ignition wire and the flame propagates back down the combustor. The flame front terminates, i.e. it uses up all of the quickest-burning flammable material in the combustor, in less than 10 ms and the flame goes out. And it is after this short flame pulse that the slower-burning analytes are excited and emit the light that is characteristic of their elements. During this period, the photomultiplier records the arrival of the analyte's light from the combustion chamber. After about 300 ms, the flame pulses again as new flammable material fills the combustion chamber from the inlet tubes and GC column and that combination once again constitutes a flammable mixture. In this way, about three flame pulses are recorded per second.

See Annex I.

B.7 Hall-electrolytic conductivity detector (ELCD or HELCD)

The effluents of the gas chromatograph are mixed with a reaction gas in a reaction tube. The resulting products are then mixed with deionised solvent. The conductivity is then measured. This detector is multi-specific (halogens, sulfur, nitrogen containing compounds), depending on the absorbing solvent selected.

B.8 Mass selective detector (MSD)

The effluents of the gas chromatograph are bombarded with electrons, which provoke bond ruptures and molecule ionization. The ions are then accelerated and placed into a magnetic field. The radii of their path is a function of their mass. Many theories describe the ionization of molecules. The ion proportions produced by different molecules are different. The detection is mass specific.

See Annex E.

B.9 Photoionization detector (PID)

The effluents of the gas chromatograph are excited by the photons of a UV lamp and ionized. The resultant charged particles are measured between two electrodes. This detector is multi-specific for different compounds, depending on the chosen lamp for excitation and ionization potentials of compounds. Only used for H_2S.

B.10 Thermoionization detector (TID)

Similar to the photoionization detector but the ionization is caused by high temperatures.

B.11 Sulfur chemiluminescence detector (SCD)

The effluents of the GC are mixed with reactive compounds and will form excited species which will relax emitting photons. Usual sulfur chemiluminescence detectors use ozone under reduced pressure. This detector is specific.

See Annex H.

B.12 Thermal conductivity detector (TCD)

The effluents of the gas chromatograph pass through a cell where a filament is heated. Another cell flushed by a reference gas homes a second filament. The two filaments are part of a Wheatstone bridge. If the effluents contain products with a different thermal conductivity than the reference gas, a current will be induced in the bridge. This signal is then measured. This detector is non-specific.

B.13 H_2S lead acetate detector

The effluents react in a high temperature hydrogenator, assuming that sulfur compounds are transformed into hydrogen sulfide. The effluents then pass through a lead acetate treated paper which will react with H_2S so produced. Optical measurement of the darkening of the tape is used to detect the sulfur compounds. This detector is specific.

Table B.1 — Detectors and their characteristics

Detector	Specificity	Detection limit	Linearity	Interferences	Main use	Remark
AED [a]	+++++[b]	++++	+++++	Unknown	Element specific	Multi-purpose
ED [a]	++++	+++	++++	Unknown	Electrolyte specific	—
ECD	variable [c]	variable [d]	++++	Possible	Halogens	Radioactive
FPD [a]	++++ to +++++	++ to ++++	++ to ++++	Hydrocarbons	Sulfur, phosphorus	Widely used
HELCD or ELCD	++++	+++	+++ to +++++	Possible	Halogens	—
MSD [a]	non-specific	+++	++ to ++++	Unknown	All organic compounds	Multi-purpose
PID	+	++++	+++++	Possible	Aromatics, inorganic compounds	—
TID	—	—	—	Possible	—	—
SCD [a]	+++++	+++++	++++	Unknown	Sulfur compounds	Low detection limit
TCD	non-specific	++	+++	Yes	—	Non-selective
H_2S lead acetate	+++++	—	—	—	—	—

+	Not very specific.
++++	Specific but can detect other non-sulfur compounds with less sensitivity.
+++++	Very specific — detects only compounds containing sulfur.

[a] Detectors used in the proficiency test.

[b] Best.

[c] Depends on the application (only H_2S or all compounds).

[d] Depends on the application (only H_2S or all compounds).

Annex C
(informative)

GC method using capillary column and FPD

C.1 Application

This method specifies the conditions for the qualitative and quantitative analysis of sulfur compounds in natural gas at a mass concentration level of 0,5 mg/m^3 up to about 600 mg/m^3 (at normal reference conditions) by gas chromatography.

An application example for this working instruction is the quality control of natural gases, including the analysis of the following components:

— Hydrogen sulfide (H_2S) (lower limit of concentration range 1 mg/m^3 at normal reference conditions);

— Carbonyl sulfide (COS);

— Methane-, ethane-, 2-methylpropane-2-thiol (tert-butyl mercaptan) (MeSH, EtSH, TBM);

— Diethyl sulfide (DES);

— Tetrahydrothiophene (THT, C_4H_8S).

C.2 Apparatus

C.2.1 Gas chromatograph, containing a capillary fused silica column (styrene-divinylbenzene polymer).

C.2.1.1 Sample injection device: gas sampling valve, capable of operating in a split/splitless mode with a sample loop of 2 ml. Set the split flow rate at 15 ml/min. To avoid adsorption and desorption phenomena, the use of metal in this part of the apparatus should be restricted.

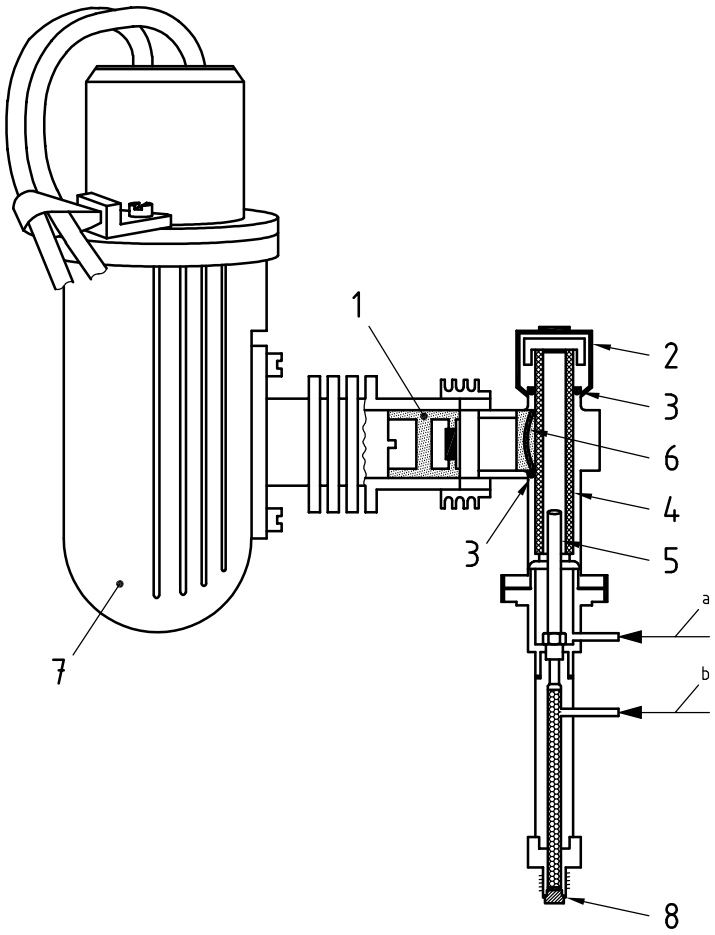
C.2.1.2 Column of fused silica, having a length of 30 m, internal diameter of 0,32 mm, and packing made of styrene-divinyl benzene polymer with a film thickness of 10 µm.

C.2.2 Flame photometric detector (FPD) (see Figure C.1)

The column effluent is mixed with hydrogen and then burned in air. Light emitted from the flame passes through a lens, a filter, and to a photomultiplier tube, which generates an electrical signal.

The FPD is used for detecting sulfur, phosphorus, or tin compounds, which produce chemiluminescent reactions with emissions at wavelengths characteristic of the S_2, HPO, and Sn species.

Sulfur radiation is at 394 nm and its intensity is approximately proportional to the square of the concentration.



Key

1 optical filter assembly
2 cap
3 O-ring
4 glass liner
5 flame jet
6 window filter assembly
7 photomultiplier tube assembly
8 column connection

a Air in.

b Hydrogen in.

Figure C.1 — Flame photometric detector (FPD)

C.3 Procedure

C.3.1 Gas flows

Apply the following values.

— Helium: 207 kPa

— Column flow rate: 1,53 ml/min

— Gas flow at detector

  1) Hydrogen: 100 ml/min

  2) Air: 95 ml/min

C.3.2 Temperatures

Apply the following temperatures.

— Oven: 70 °C for 4 min

— Heating rate: 5 °C / min

— Final temperature: 200 °C for 5 min

— Injector: 150 °C

— Detector: 375 °C

C.3.3 Elution times

These shall be the following.

— Hydrogen sulfide: 2,44 min

— Carbonyl sulfide: 3,30 min

— Methanethiol: 8,76 min

— Ethanethiol: 15,58 min

— 2-Methylpropane-2-thiol: 24,39 min

— Diethyl sulfide: 27,91 min

— Tetrahydrotiophene: 30,88 min

— Duration of analysis: 35 min

C.4 Calculation

The relationship between the FPD response and the sulfur concentration is given by

$$A = k\,C^{n} \tag{C.1}$$

where

A is the signal of the component peak;

k is a constant;

C is the mass concentration;

n is the exponent.

Equation (1) can be rearranged to

$$\lg A = \lg k + n \lg C \tag{C.2}$$

For most accurate results, the exponent n must be determined with at least two standard gases containing the component of interest at 2 levels of concentration: the first at 20 % (C_1) of the full scale mass concentration and the second at 80 % (C_2). Then n is defined as

$$n = \frac{\lg \frac{A_1}{A_2}}{\lg \frac{C_1}{C_2}} \tag{C.3}$$

where

A_1 is the signal of the component peak at 20 % of the full scale;

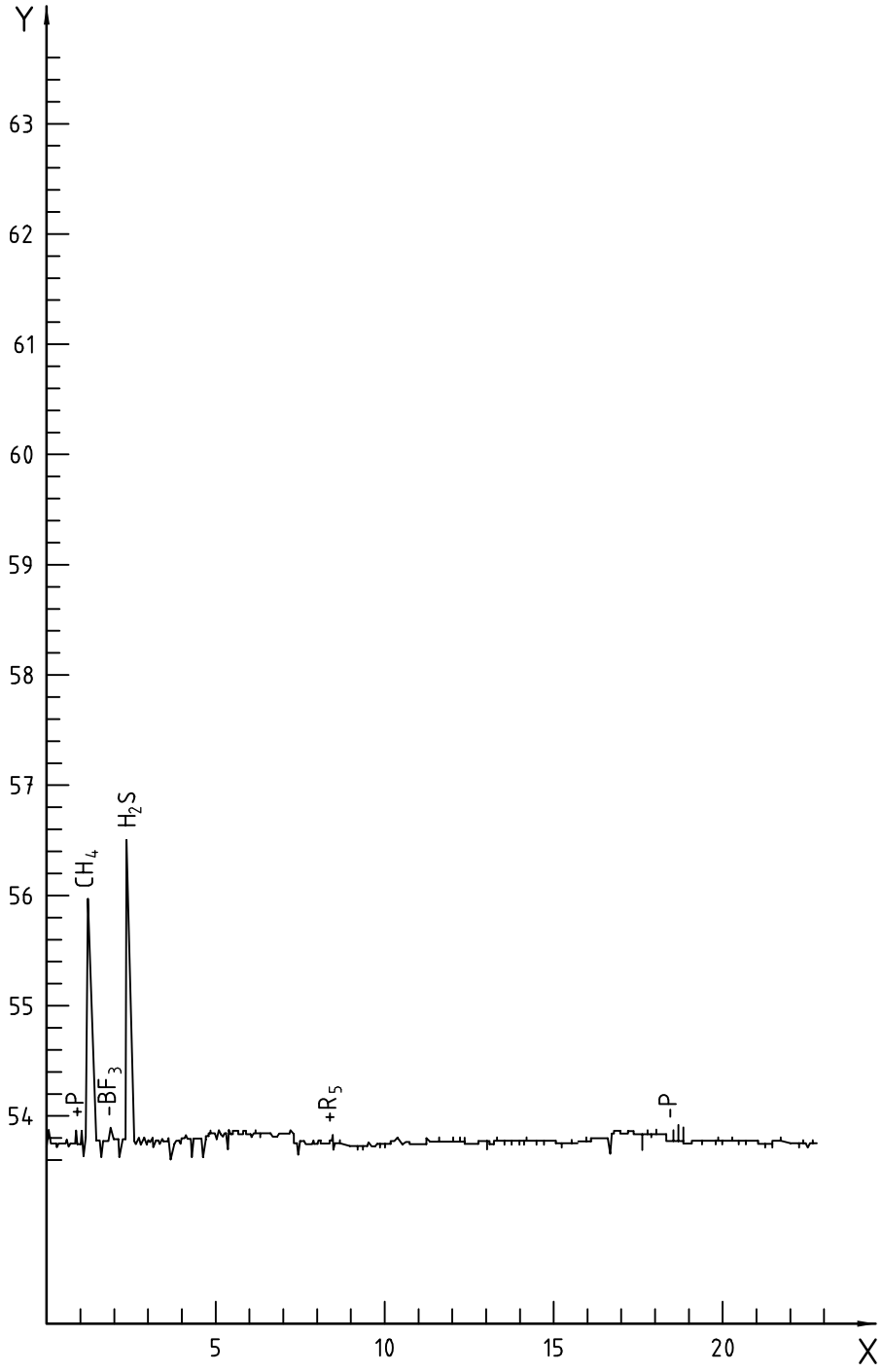
A_2 is the signal of the component peak at 80 % of the full scale.

and

$$k = \frac{A_2}{{C_2}^{n}} \tag{C.4}$$

The n and k values can then be used to determine the mass concentration of the sample according to Equation (C.1).

The relationship between detector response and concentration is not linear (but the concentration is proportional to the square root of the area). Therefore, a calibration mixture shall be used in which the mass concentration of each component is close to the mass concentration of the same component in the sample to be analysed.

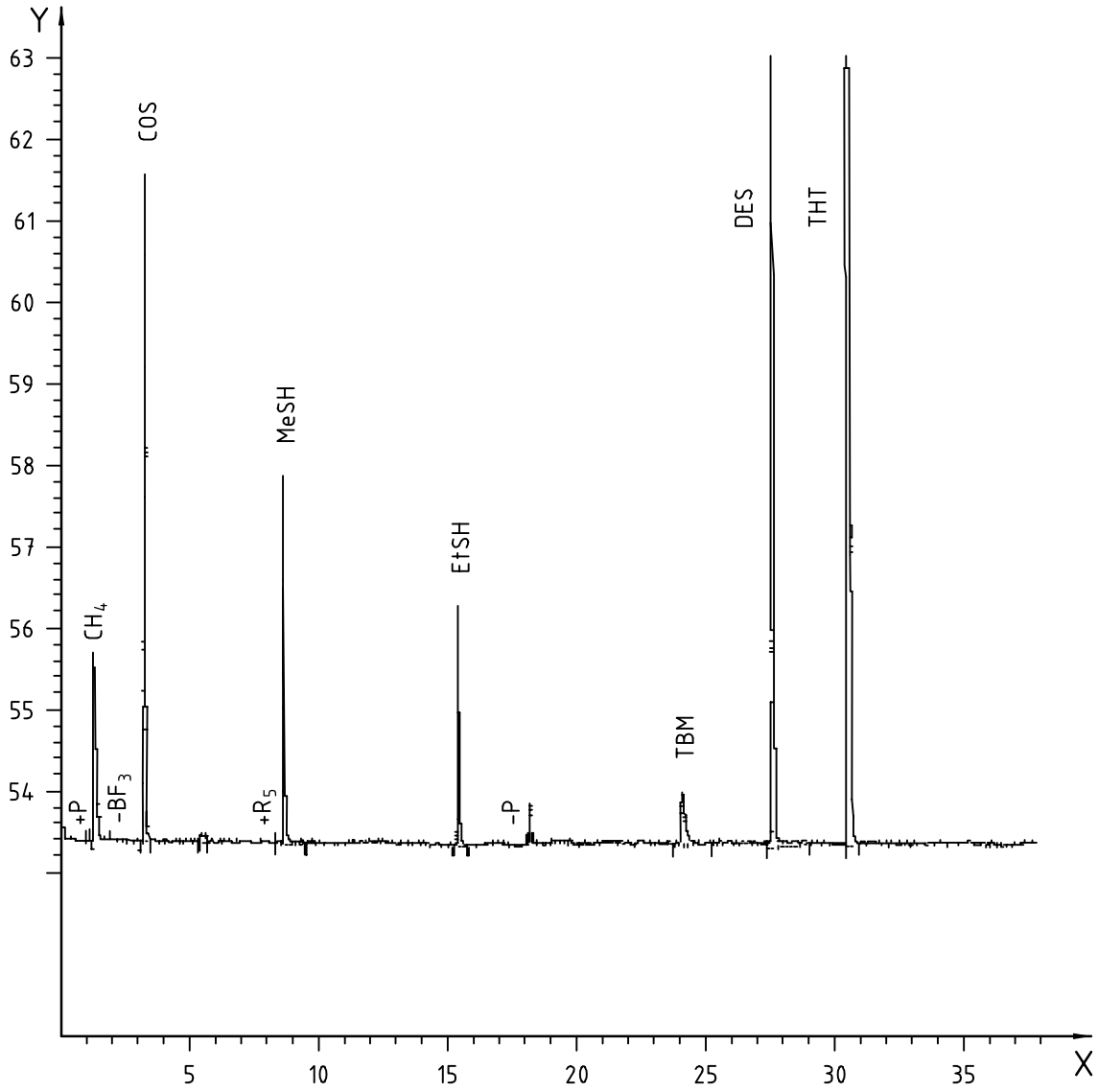


Key

X time, min

Y response

Figure C.2 — Chromatogram of Mixture 1 (H_2S in methane)



Key

X time, min

Y response

Figure C.3 — Chromatogram of Mixture 2 (COS, MeSH, EtSH, TBM, DES, THT in methane)

Annex D
(informative)

GC method using ED

D.1 Application

The method is applicable to the following compounds:

— hydrogen sulfide;

— methane-, ethane-, propane-, 2-methylpropane-2-thiol (tert-butyl mercaptan) (MeSH, EtSH, *n*-PrSH, TBM);

— tetrahydrothiophene.

It is not applicable for the determination of carbonyl sulfide.

Under normal conditions of application, this method can be used to determine the content of each compound within a mass concentration range of from 0,1 mg to 100 mg, with the mass concentration expressed in milligrams of sulfur per cubic metre of gas at standard pressure and temperature. Usually, application range for equivalent THT is 15 mg to 40 mg per cubic metre of gas.

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

NOTE The chromatographic conditions described enable hydrogen sulfide 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 performance of the chromatographic column can be improved to increase this ratio.

D.2 Apparatus

Two different apparatus based on the same detection principle may be used to conduct the analysis in either 50 min (Apparatus 1) or 10 min (Apparatus 2), using column switching. The two apparatus operate at room temperature and consist essentially of four parts.

D.2.1 Sample injection device: to avoid adsorption and desorption phenomena, the use of metal in this part of the apparatus shall be restricted.

D.2.1.1 Manual injection: the sample is taken using a gas syringe, and immediately injected through a PTFE-coated rubber septum at the top of the column.

D.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).

D.2.2 Columns.

D.2.2.1 One glass column (Apparatus 1) set up as shown in Figure D.1 and as follows.

— Length: 40 cm

— Internal diameter: 4 mm

— Packing (support): Chromosorb W, with particle size of 150 µm to 180 µm (80 to 100 mesh, Tyler series)

— Packing (in stationary phase):

1) for the first two-thirds of the column length, silicone DC 200, 40 g per 100 g of support;

2) for the last third, dinonyl phthalate, 40 g per 100 g of support.

D.2.2.2 Three glass columns (Apparatus 2) set up as shown in Figure D.2 and as follows.

D.2.2.2.1 Column 1

— Length: 25 cm

— Internal diameter: 4 mm

D.2.2.2.2 Column 2

— Length: 140 cm

— Internal diameter: 4 mm

D.2.2.2.3 Column 3

— Length: 18 cm

— Internal diameter: 4,7 mm

D.2.2.2.4 Packing (support): Chromosorb W[1)], with particle size of 150 µm to 180 µm (80 to 100 mesh, Tyler series).

D.2.2.2.5 Packing (in stationary phase): silicone OV 101 20 g per 100 g of support.

D.2.3 Three electrochemical detectors (ED): one for Apparatus 1 and two for Apparatus 2 (see Figure D.2).

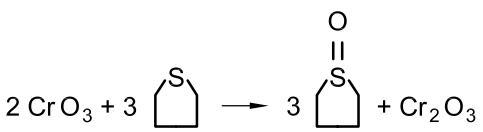
Each detector consists of a glass or methyl polymethacrylate container. The electrodes, two pieces of platinum gauze arranged in parallel as grids (diameter 35 mm, 3 600 wires per cm^2), are welded 30 mm apart in a borosilicate glass tube and separately connected to the amplifier or to the recorder by a platinum wire.

The electrolyte, a solution of chromium(VI) oxide in distilled water (0,66 mol/l), 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 sulfur compound occurs, a redox-reaction occurs on the electrode surface creating a potential difference between the two electrodes, thus causing a current, which is measured in a low-resistance measuring circuit.

EXAMPLE Tetrahydrothiophene (THT) is oxidized to tetramethylene sulphoxide according to the general reaction:



1) Chromosorb® W is an example of a product available commercially. This information is given for the convenience of users of this part of ISO 11933 and does not constitute an endorsement by ISO of this product.

The detector is sensitive to sudden temperature changes. It shall therefore be placed in surroundings with a constant temperature, or, even 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 the mass concentration of sulfur compounds.

D.3 Procedure

D.3.1 Preparation of Apparatus 1

D.3.1.1 Carrier gas

This shall be nitrogen at a pressure of approx. 2×10^5 Pa (2 bar) and a flow rate of 100 ml/min at 293 K (20 °C).

D.3.1.2 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.

D.3.2 Preparation of Apparatus 2

D.3.2.1 Carrier gas

This shall be as follows.

a) Path A — carrier gas for THT determination: nitrogen at a pressure of approx. 1×10^5 Pa (2 bar) and a flow rate of 150 ml/min at 293 K (20 °C).

b) Path B — carrier gas for thiols determination: nitrogen at a pressure of approx. $1{,}6 \times 10^5$ Pa (1,6 bar) and a flow rate of 80 ml/min at 293 K (20 °C).

D.3.2.2 Automatic injection

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

D.3.3 Analysis

Inject 20 ml of the sample, irrespective of the injection device used. This is the maximum volume and may be reduced when the mass concentration of sulfur compounds is high.

D.3.4 Elution times

D.3.4.1 Apparatus 1

If the operation is automatic, the duration of the analysis cycle, including the injection and elution stages, is about 1 h.

The order and elution time for various constituents at 20°C for a flow rate of 100 ml/min shall be the following.

— Hydrogen sulfide (for manual operation only): 30 s

— MeSH: 60 s

— EtSH: 80 s

— 2-Propanethiol: 160 s

— 2-Methylpropane-2-thiol: 240 s

— 1-Propanethiol: 290 s

— 2-Butane thiol: 560 s

— Tetrahydrothiophene: 2 100 s

— Duration of analysis: 45 min

In order to reduce the total time of the analysis, the elution of tetrahydrothiophene may also be accelerated by increasing the flow rate of the carrier gas, after the elution of butane-2-thiol, from 100 ml/min to 500 ml/min by means of an automatic device. The total time of analysis is only 15 min whilst still using only a single injection.

D.3.4.2 Apparatus 2

If the operation is automatic, the duration of the analysis cycle, including the injection and elution stages, is about 10 min.

The order and elution time for the various constituents at 298 K (20 °C) at the above-mentioned conditions shall be the following.

a) Path A: tetrahydrothiophene: 320 s

b) Path B

— Hydrogen sulfide (for manual operation only): 30 s

— MeSH: 80 s

— EtSH: 125 s

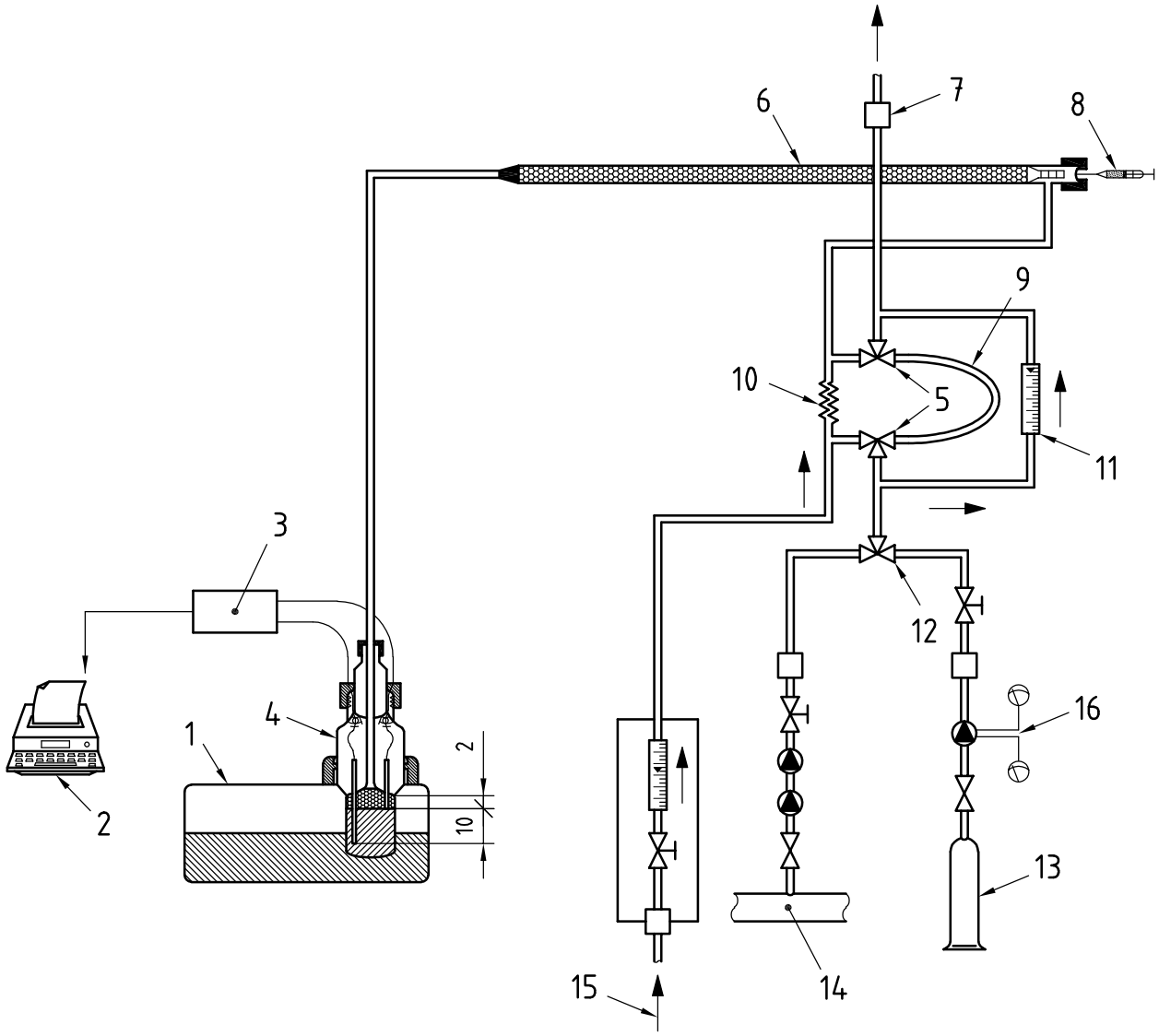
— 2-Propanethiol: 140 s

— 2-Methylpropane-2-thiol: 220 s

— 1-Propanethiol: 260 s

— 2-Butane thiol: 430 s

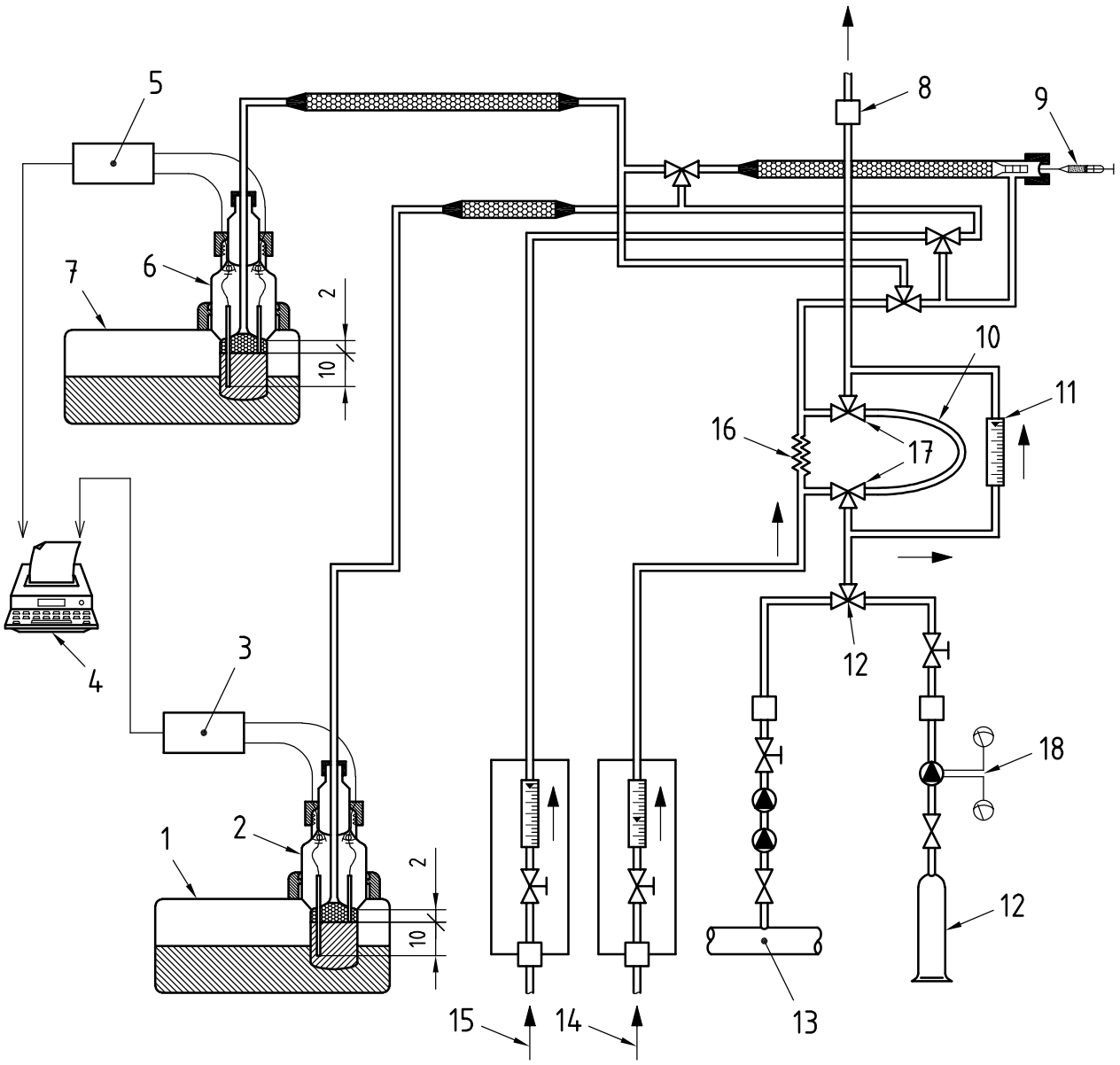
— Duration of analysis: 10 min



Key

1	tank	9	sampling loop
2	integrator	10	restrictor
3	signal to integrator	11	rotameter
4	detector	12	selection electromagnetic valve
5	electromagnetic valves	13	calibration gas
6	chromatographic column RSH + THT	14	sample to be analysed
7	vent	15	carrier gas
8	manual injection	16	needle valve

Figure D.1 — Apparatus 1



Key

1 tank
2 THT detector
3 signal to integrator
4 integrator
5 signal to integrator
6 RSH detector
7 tank
8 vent
9 manual injection
10 sampling loop
11 rotameter
12 calibration gas
13 sample to be analysed
14 RSH carrier gas
15 THT carrier gas
16 restrictor
17 electromagnetic valves
18 needle valve

Figure D.2 — Apparatus 2

Annex E
(informative)

GC method using MSD

E.1 Application

The method is applicable to the following compounds:

— hydrogen sulfide (H_2S);

— carbonyl sulfide (COS);

— methane-, ethane-, 2-methylpropane-2-thiol (tert-butyl mercaptan) (MeSH, EtSH, TBM);

— diethyl sulfide (DES);

— tetrahydrothiophene (THT, C_4H_8S).

Under normal conditions of application, this method can be used to determine the content of each compound within a mass concentration range of from 0,1 mg to 100 mg (mass concentration expressed in milligrams of sulfur) per cubic metre of gas at standard pressure and temperature. Usually, the application range for equivalent THT is 15 mg to 60 mg per cubic metre of gas.

The detector can be configured such that it is not sensitive to the major components of natural gases.

E.2 Apparatus

A gas chromatograph containing a capillary-fused silica column (cross-linked methylsilicone gum) and a mass selective detector.

E.2.1 Sample injection device.

E.2.1.1 Gas sampling valve with a sample loop of 0,3 ml. To avoid adsorption and desorption phenomena, the use of metal in this part of the apparatus shall be restricted.

E.2.1.2 Automatic injection by means of a programmer that 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).

E.2.1.3 Column of fused silica and length 50 cm, with internal diameter of 0,2 mm and packing of cross-linked silicone gum of a film thickness of 0,5 µm.

E.2.2 Mass selective detector (MSD), containing an electron impact ion source, a hyperbolic quadrupole mass filter, an electron multiplier detector, four electronics boards, a power supply, an oil diffusion pump and a mechanical foreline pump.

Data system software includes programs to calibrate the MS, acquire data and process data. The calibration programs can adjust voltages in the ion source, calibrate mass assignments and control the scanning of the mass analyser. In addition, the data acquisition system allows monitoring of the total ion current or the particular ion (in selected ion monitoring mode).

EXAMPLE Tetrahydrothiophene is bombed by the electron impact ion source and fragmented as follows:

$THT + e^+ > CH_2 - CH_2 - S$ (base peak)

E.3 Procedure

E.3.1 Preparation of apparatus

E.3.1.1 Carrier gas

This shall be helium (at least 99,995 %) at a pressure of approx. 2×10^5 Pa (2 bar) and a flow rate of 12 ml/min at 293 K (20 °C).

E.3.1.2 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.

E.3.2 Analysis

Inject 0,3 ml of the sample using the injection device.

E.3.3 Elution times

The order of elution for various constituents at 20 °C for a flow rate of 12 ml/min shall be the following.

— H_2S: 2,93 min

— COS: 3,59 min

— MeSH: 10,90 min

— EtSH: 19,02 min

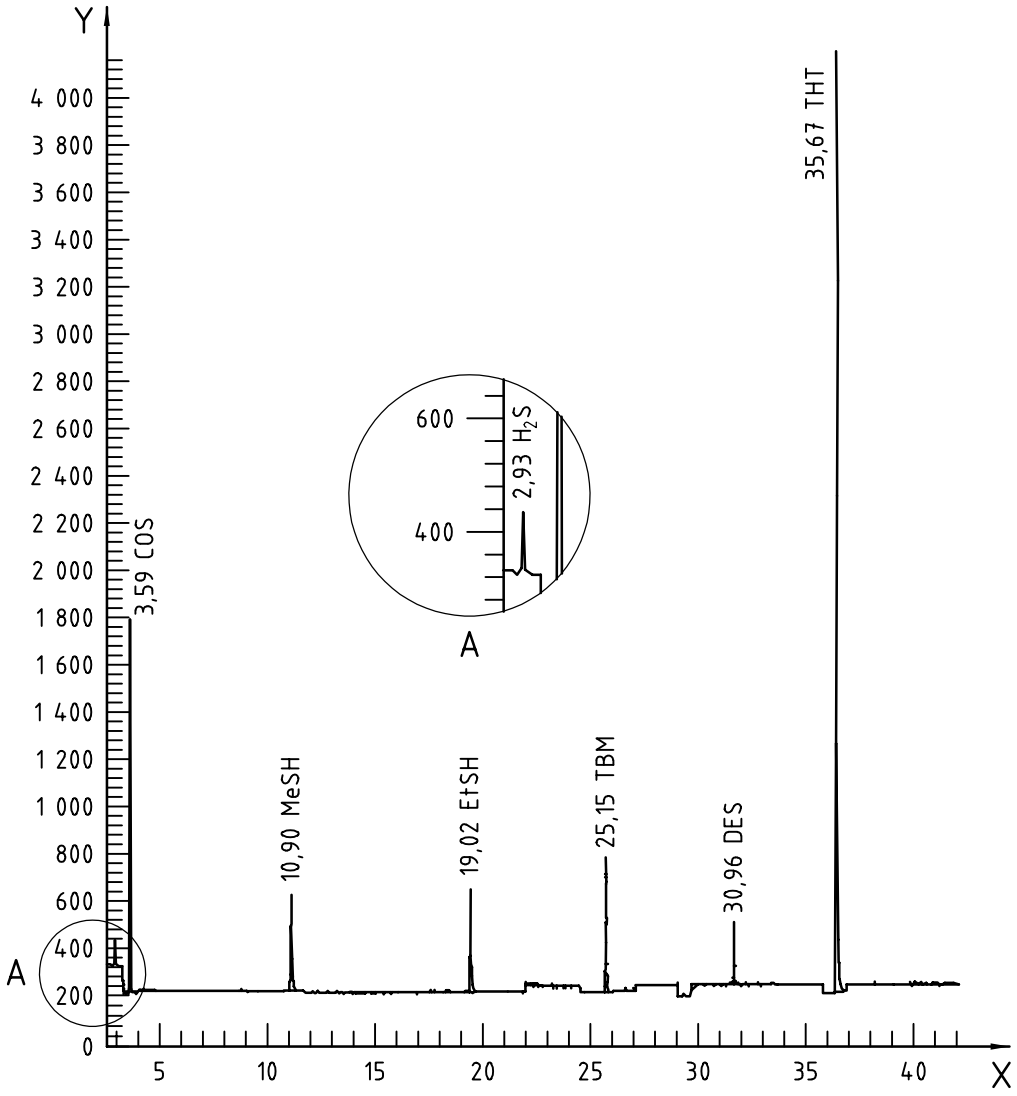
— TBM: 25,15 min

— DES: 30,96 min

— THT: 35,67 min

In order to reduce the total time of the analysis, the elution of tetrahydrothiophene may also be accelerated by increasing the temperature to 120 °C. Hydrogen sulfide and carbonyl sulfide will be not separated.

See Figure E.1.



Key

X time, min

Y abundance

Figure E.1 — Chromatogram of Mixture 2 (COS, MeSH, EtSH, TBM, DES, THT in methane)

Annex F
(informative)

GC method using AED

F.1 Application

The method is applicable to the following compounds:

— hydrogen sulfide (H_2S);

— carbonyl sulfide (COS);

— methane-, ethane-, 2-methylpropane-2-thiol (tert-butyl mercaptan) (MeSH, EtSH, TBM);

— diethyl sulfide (DES);

— tetrahydrothiophene (THT, C_4H_8S).

F.2 Apparatus

F.2.1 Capillary column gas chromatograph equipped with temperature and column pressure programming facilities and an atomic emission detector (AED), and fitted with a gas injection valve capable of being operated in a pulsed split/splitless mode.

F.2.2 Two capillary, fused-silica columns, coupled to give a column 100 m in length.

F.2.2.1 Column 1

— Length: 50 m

— Internal diameter: 0,32 mm

— Packing: CP-Sil 5 with a film thickness of 5 µm

F.2.2.2 Column 2

— Length: 50 m

— Internal diameter: 0,32 mm

— Packing: CP-Sil 5 with a film thickness of 10 µm

F.3 Procedure

F.3.1 Preparation of apparatus

F.3.1.1 Oven

Apply the following conditions.

— Initial temperature: 40 °C

— Initial time: 15 min

— Programming rate: 15 °C/min

— Final temperature: 230 °C

— Final time: 12 min

F.3.1.2 Pressure

Apply the following conditions.

— Initial pressure: 150 kPa

— Initial time: 12,5 min

— Programming rate: 68 kPa/min

— Final pressure: 285,7 kPa

F.3.2 Injection

This shall be as follows.

— Pulsed split injection heating: 130 °C

— Pressure: 150 kPa

— Injection pulse: 170 kPa for 0,6 min

— Split ratio: 3 :1

— Gas saver: 2 min to 15 ml/min total helium flow

F.3.3 Atomic emission detector

The emission lines of the AED checked are the three lines at about 181 nm (nominal) with scavenger gases O_2 and H_2, the minimum detectable amount is 1,0 pg/s, selectivity vs. carbon is about 30 000.

F.4 Elution times

These shall be the following.

— H_2S: 10,8 min

— COS: 11,6 min

— MeSH: 15,2 min

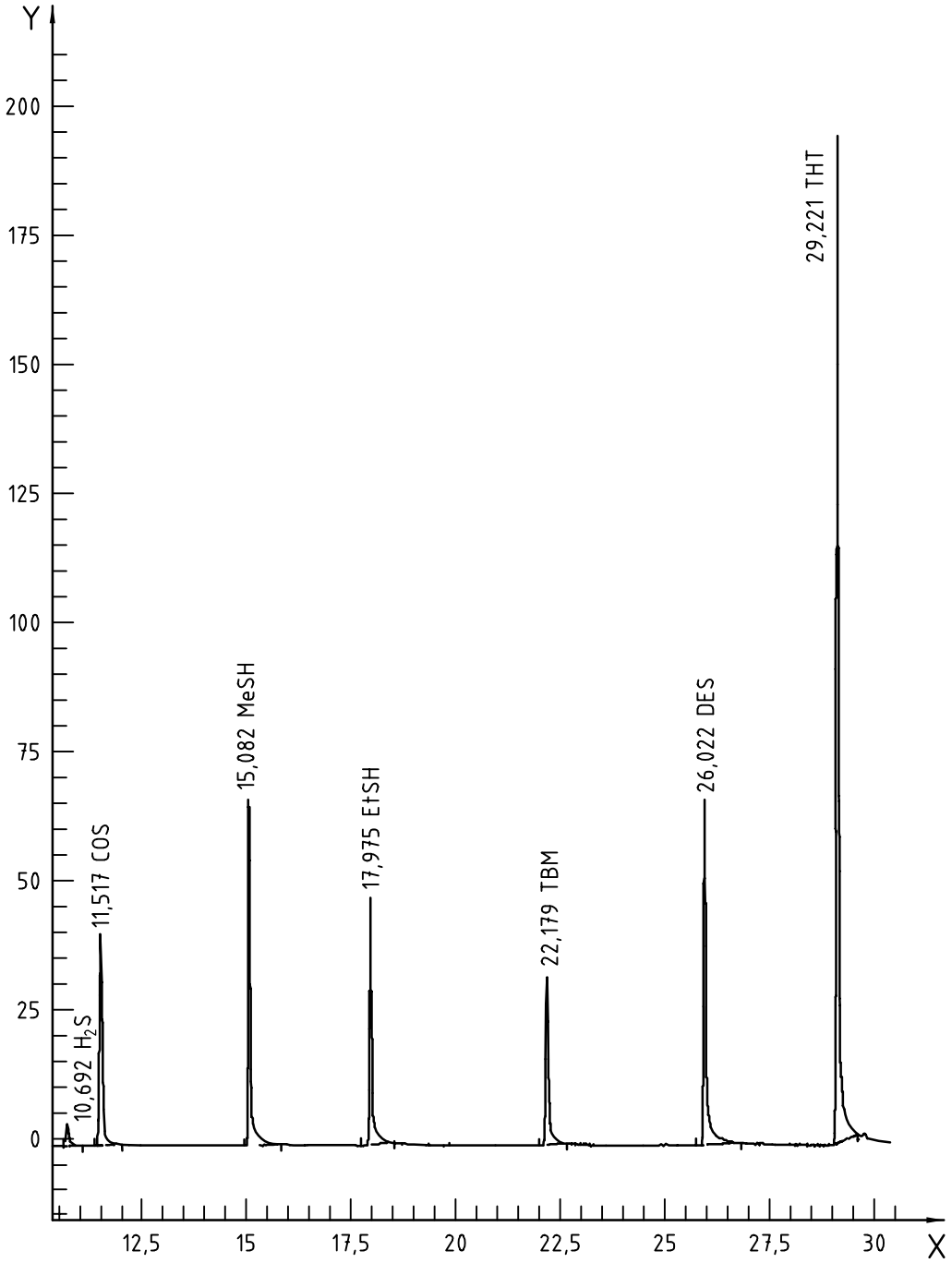
— EtSH: 18,1 min

— TBM: 22,3 min

— DES: 26,2 min

— THT: 29,4 min

— Total analysis time: 40 min



H_2S traces, COS 5 mg/m^3, MeSH 5 mg/m^3, EtSH 5 mg/m^3, TBM 6 mg/m^3, DES 10 mg/m^3, THT 25 mg/m^3

Key

X time, min

Y counts

Figure F.1 — Chromatogram of Mixture 2

Annex G
(informative)

GC methods using column switching and FPD

G.1 Application

The methods are applicable to the following compounds:

— hydrogen sulfide (H_2S);

— carbonyl sulfide (COS);

— methane-, ethane-, 2-methylpropane-2-thiol (tert-butyl mercaptan) (MeSH, EtSH, TBM);

— diethyl sulfide (DES);

— tetrahydrothiophene (THT, C_4H_8S).

G.2 Apparatus

These methods use a standard packed column gas chromatograph equipped with temperature-programming facilities and a flame photometric detector (FPD). The latter is operated at 150 °C in the single-flame mode, as described in [5]. The chromatograph is fitted with dual-channel flow controls for carrier gas (helium) and single-channel flow controls for the detector gases (hydrogen and air).

G.2.1 Three packed, stainless-steel columns placed in a chromatographic oven: an OV17 analytical column (Column 1), a short Porapak[2)] QS precolumn, and a longer Porapak QS analytical column (Column 2), in accordance with Figures G.1 and G.2 and the following.

G.2.1.1 (Analytical) Column 1

— Length: 180 cm

— Outside diameter: 3 mm

— Packing: 20 % m/m OV17 on Chromosorb[2)] W and particle size 100 to120 mesh

G.2.1.2 Precolumn

— Length: 30 cm

— Outside diameter: 3 mm

— Packing: acetone-washed Porapak QS and particle size 80 to 100 mesh

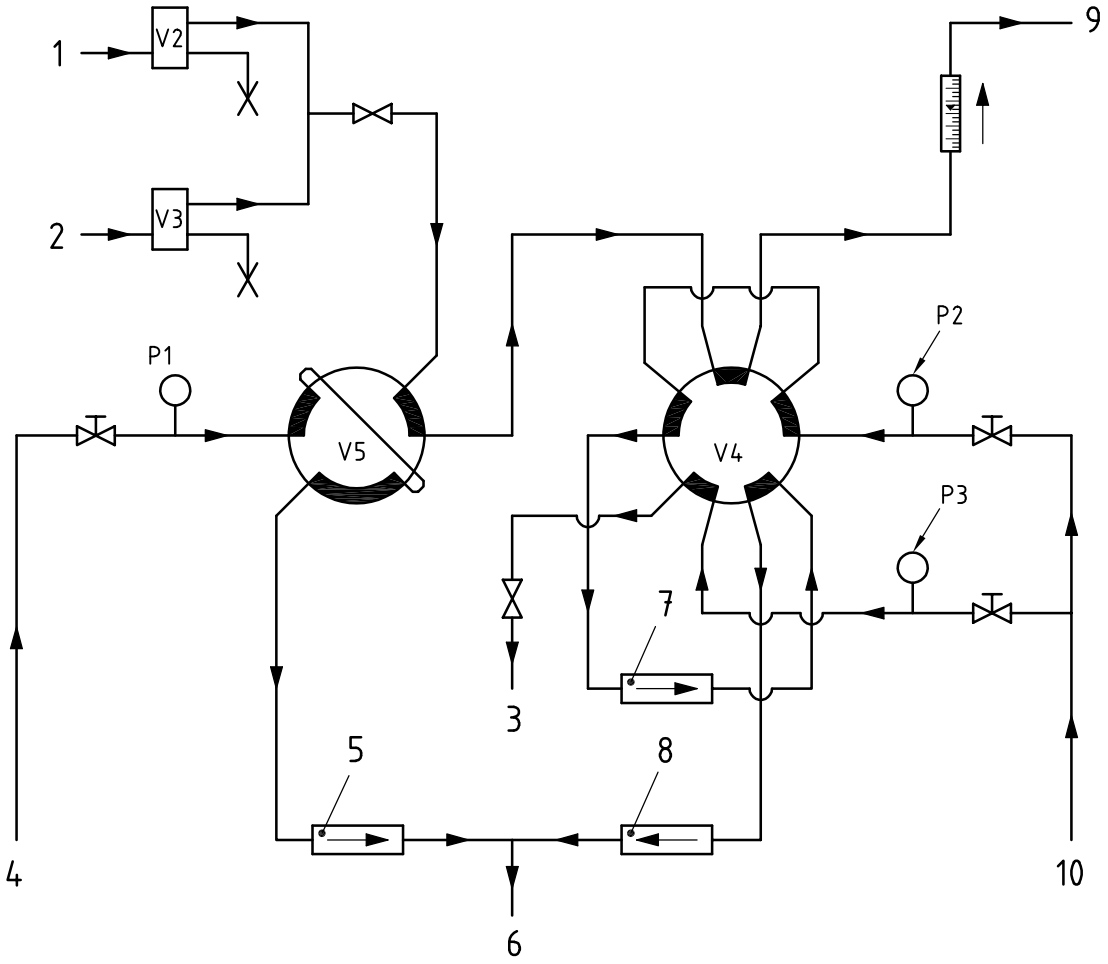
2) Porapak and Chromosorb are examples of products available commercially. This information is given for the convenience of users of this part of ISO 11933 and does not constitute an endorsement by ISO of these products.

G.2.1.3 (Analytical) Column 2

— Length: 180 cm

— Outside diameter: 3 mm

— Packing: acetone-washed Porapak QS, and particle size 80 to 100 mesh

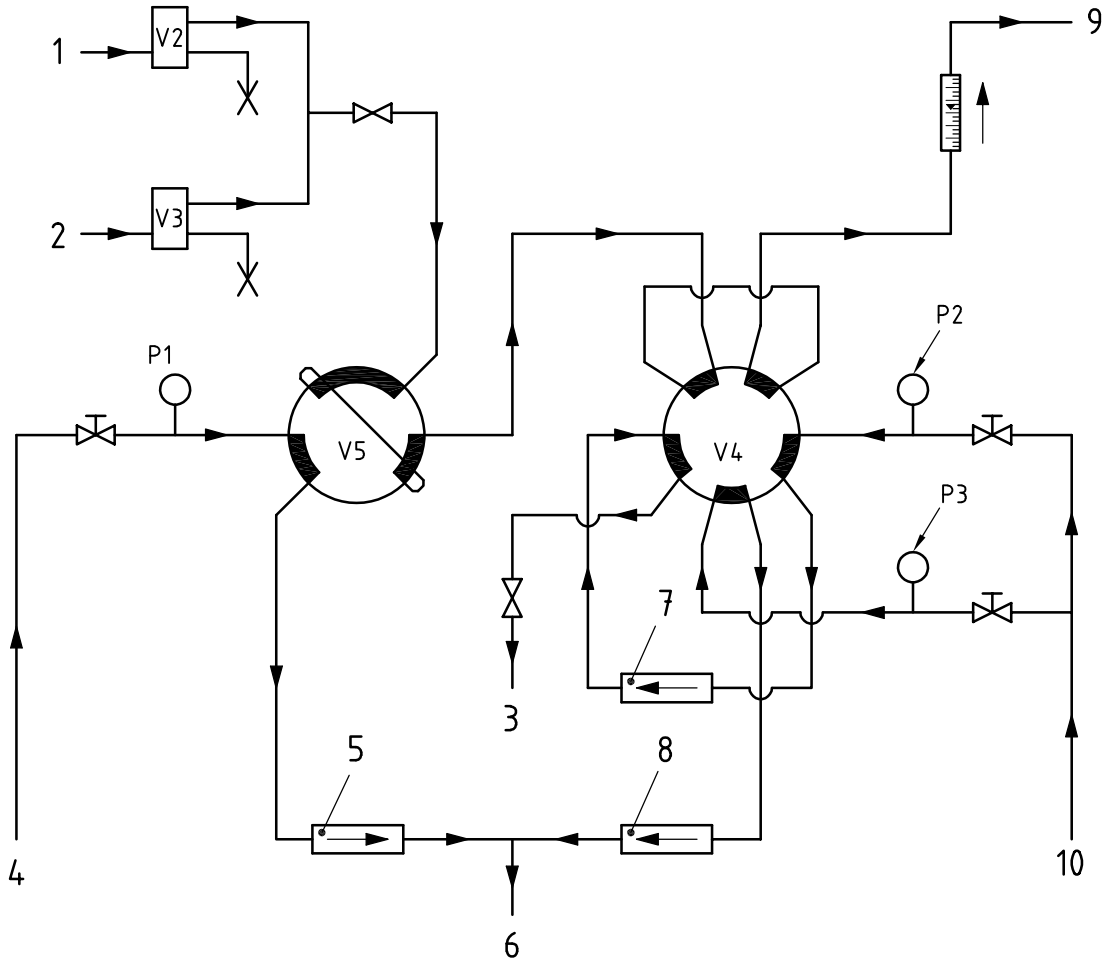


Key

1 sample
2 calibration gas
3 backflush vent
4 carrier 1
5 OV17 column
6 FPD
7 Porapak QS precolumn
8 Porapak QS column
9 sample/calibration gas vent
10 carrier 2

V2, V3, V4, V5 see G.2.2

Figure G.1 — Schematic of sulfur chromatograph — Sample injection mode



Key

1 sample
2 calibration gas
3 backflush vent
4 carrier 1
5 OV17 column
6 FPD
7 Porapak QS precolumn
8 Porapak QS column
9 sample/calibration gas vent
10 carrier 2

V2, V3, V4, V5 see G.2.2

Figure G.2 — Schematic of sulfur chromatograph — Backflush mode

G.2.2 Valves

These are as follows.

V2 (optional): switches sample flow on and off

V3 (optional): switches calibration gas on and off

V4: 10-port automatic gas sampling valve

V5: 6-port automatic gas sampling valve

G.2.3 Configuration

The two Porapak QS columns are connected to the 10-port gas sampling valve. This valve is configured so that, in the inject position, sample gas is injected onto the Porapak QS pre-column connected in series with the Porapak QS analytical column and, in the load position, the Porapak QS precolumn is backflushed to vent while the Porapak QS analytical column continues to be eluted to the detector. Under normal isothermal conditions, the Porapak QS column (with pre-column backflush) separates hydrogen sulfide and carbonyl sulfide.

The OV17 column is connected to the 6-port automatic gas sampling valve. This valve is configured conventionally to inject sample gas onto the OV17 column. Under normal isothermal conditions, the OV17 column separates ethanethiol, *2*-methylpropane-2-thiol, methyl ethyl sulfide and diethyl sulfide.

The two valves should be mounted in the chromatographic oven. Both valves should be fitted with sample loops made from 6 mm O.D. PTFE tube. Sample loop size will need to be matched to analytical requirements, but typically loop sizes of 2 ml to 5 ml are used. The sample loops are connected in series so that both loops can be purged at the same time.

The outlet of the OV17 column and the outlet of the Porapak QS analytical column are joined together at a T-piece so that the combined column flows enter the FPD detector.

The Porapak QS column flow should be 170 ml/min with a delivery pressure of 340 kPa.

The OV17 column flow should be 100 ml/min with a delivery pressure of 340 kPa.

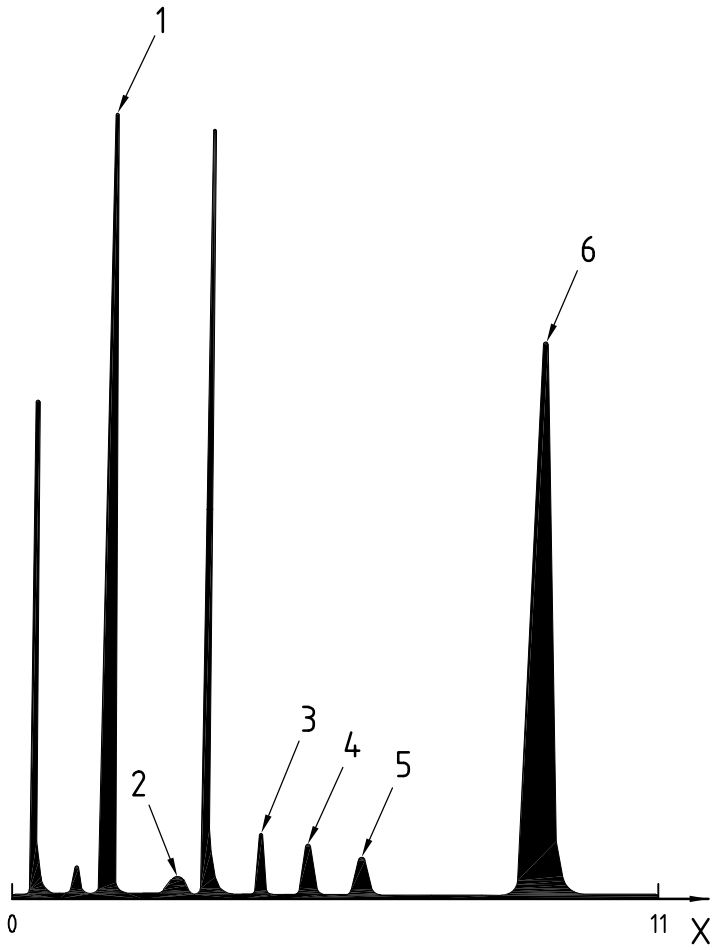
G.3 Procedures

Four isothermal analytical and three temperature-programmed analytical methods may be used.

a) **Method 1** measures H_2S, COS, EtSH, TBM, MeSH and DES isothermally at 50 °C. Figure G.3 is a chromatogram obtained using Method 1. Make two sample injections.

   1) Make the first sample injection using the 10-port valve (V4). Use the long Porapak QS column to separate the hydrogen sulfide and COS. Backflush heavier components from the short Porapak QS precolumn.

   2) Three minutes later, after elution of hydrogen sulfide and COS, make a second sample injection using the 6-port valve (V5). Separate ethanethiol, 2-methylpropane-2-thiol, methyl ethyl sulfide and diethyl sulfide on the OV 17 column. The analysis cycle is about 11 min.



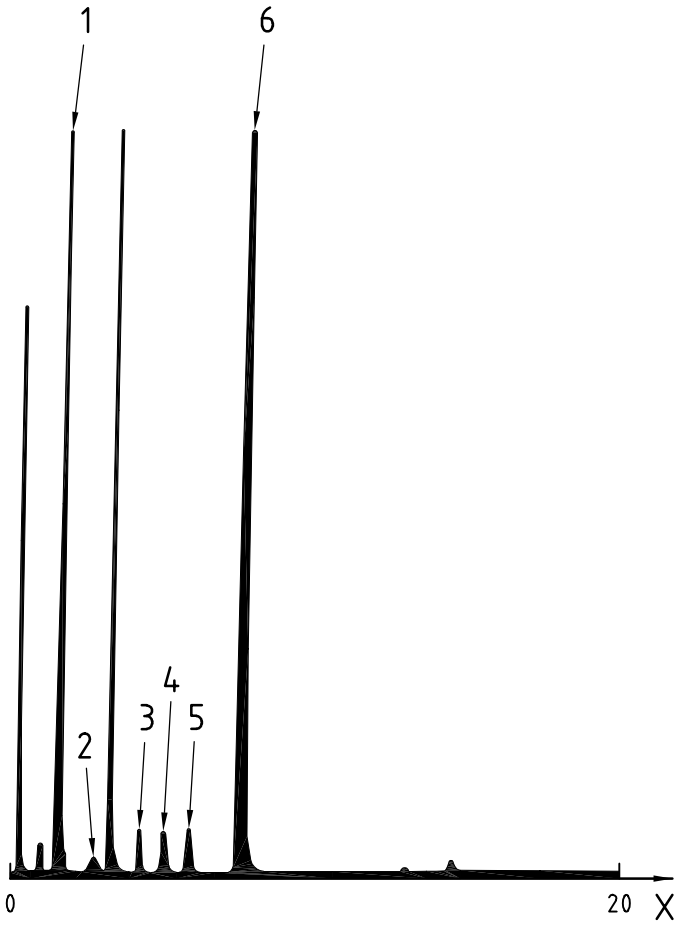
Key

X time, min

1 H_2S (4,3 mg/m^3)
2 COS (not determined)
3 EtSH (0,24 mg/m^3)
4 TBM (0,48 mg/m^3)
5 MeSH (0,43 mg/m^3)
6 DES (2,9 mg/m^3)

Figure G.3 — Chromatogram using Method 1

b) **Method 2** is a temperature-programmed version of Method 1, which extends the range of measurement to include numerous other components such as tetrahydrothiophene and organic disulfides. It measures H_2S and COS isothermally at 50 °C, as above. Inject the second sample onto the OV17 column at 50 °C but, after isothermal elution of EtSH and TBM, program the OV17 column temperature to 150 °C at 10 °C/min. Figure G.4 is a chromatogram obtained using Method 2. The analysis cycle is about 30 min (20 min analysis + 10 min cool-down).



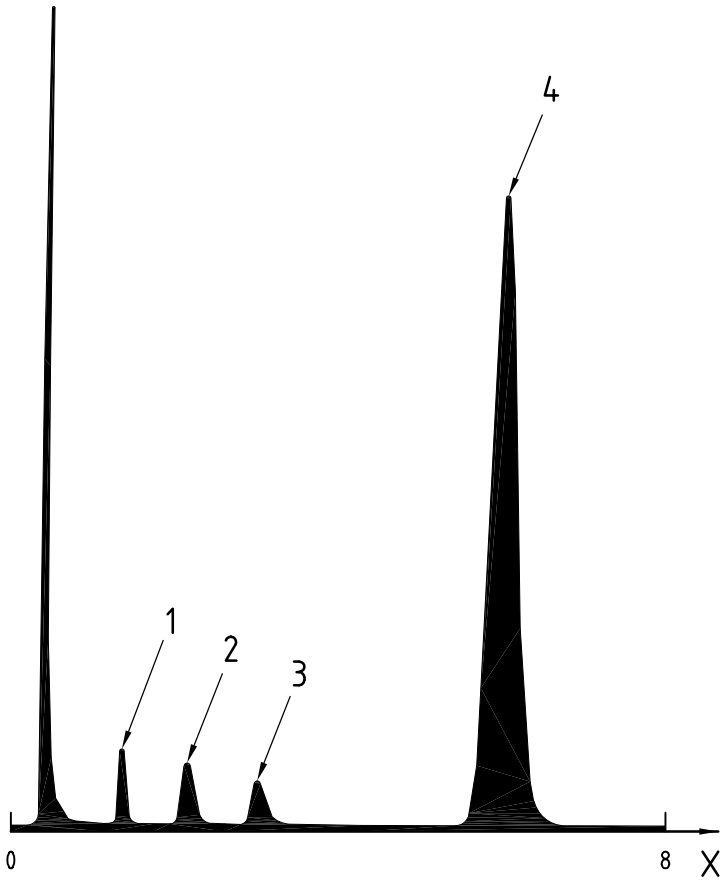
Key

X time, min

1 H_2S (4,3 mg/m^3)
2 COS (not determined)
3 EtSH (0,24 mg/m^3)
4 TBM (0,48 mg/m^3)
5 MeSH (0,43 mg/m^3)
6 DES (2,9 mg/m^3)

Figure G.4 — Chromatogram using Method 2

c) **Method 3** is the classical odorant analysis method first introduced in the original automatic odorant analyser. It measures EtSH, TBM, MeSH and DES isothermally at 50 °C, using the OV17 column. Figure G.5 is a chromatogram obtained using Method 3. Make a single sample injection using the 6-port valve (V5). The analysis cycle is circa 8 minutes.



Key

X time, min

1 EtSH (0,24 mg/m^3)

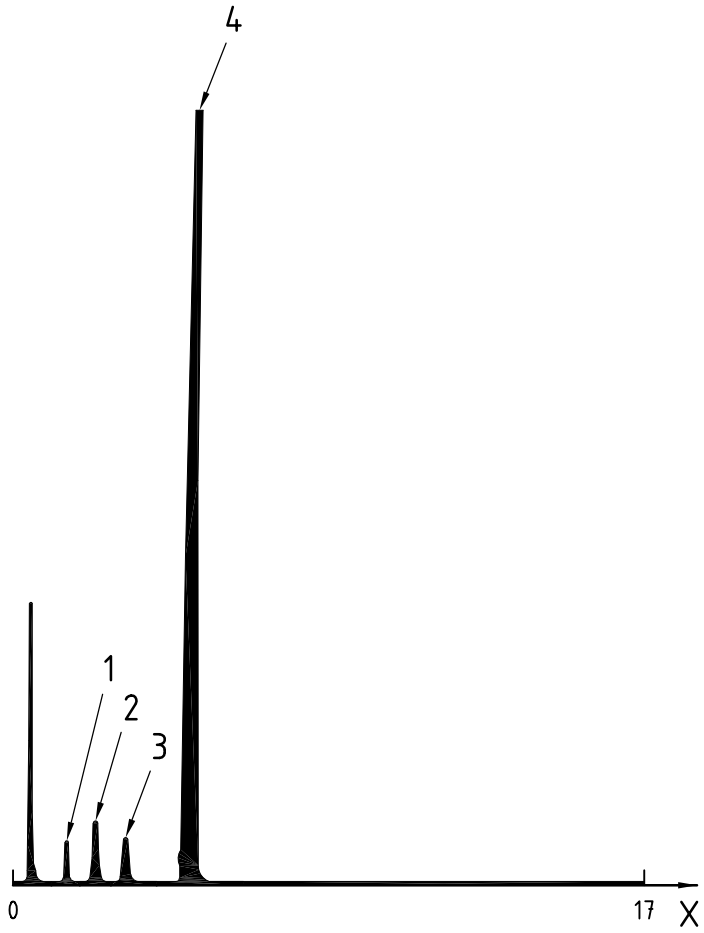
2 TBM (0,48 mg/m^3)

3 MeSH (0,43 mg/m^3)

4 DES (2,9 mg/m^3)

Figure G.5 — Chromatogram using Method 3

d) **Method 4** is a temperature-programmed version of Method 3. After isothermal elution of EtSH and TBM at 50 °C, program the OV17 column temperature to 150 °C at 10 °C/min. Figure G.6 is a chromatogram obtained using Method 4. The analysis cycle is about 25 min. Method 4 is also able to be used to measure heavier components where present.



Key

X time, min

1 EtSH (0,46 mg/m^3)

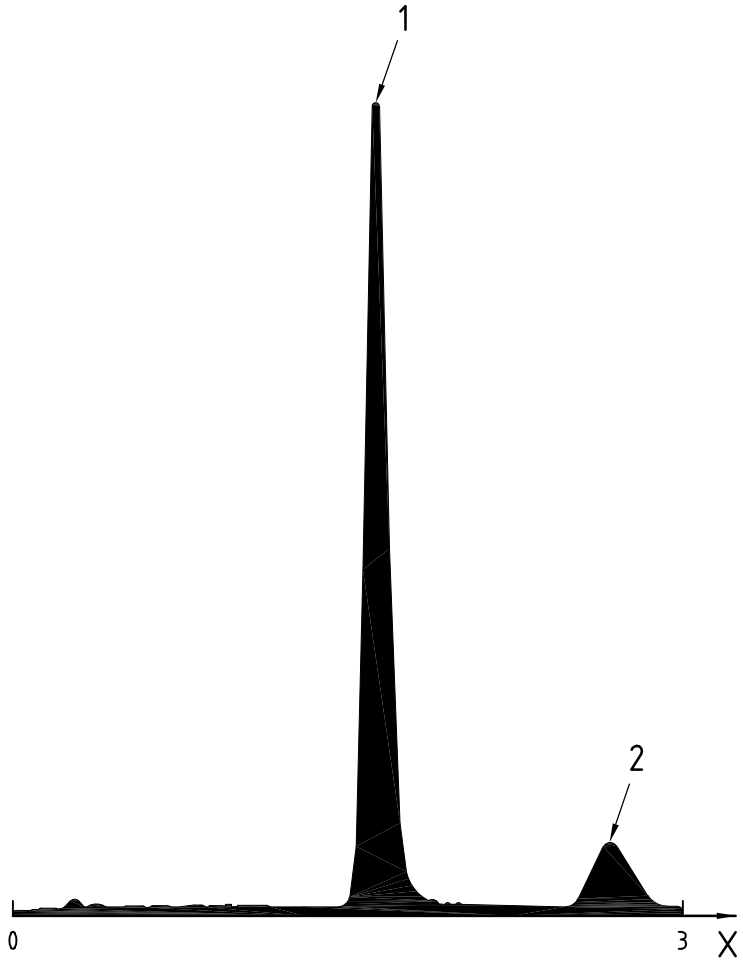
2 TBM (1,02 mg/m^3)

3 MeSH (0,87 mg/m^3)

4 DES (7,0 mg/m^3)

Figure G.6 — Chromatogram using Method 4

e) **Method 5** uses the two Porapak QS columns to measure H_2S and COS isothermally at 50 °C. Figure G.7 is a chromatogram obtained using Method 5. Use the 10-port valve (V4) to inject sample onto the Porapak QS pre-column, initially in series with the Porapak QS analytical column. After passing H_2S and COS from the Porapak QS pre-column to the Porapak QS analytical column, return V4 to the "sample load" position and backflush to vent all higher components remaining on the Porapak QS pre-column. Then separate H_2S and COS and elute from the Porapak QS analytical column. The analysis cycle is circa 3 min.



Key

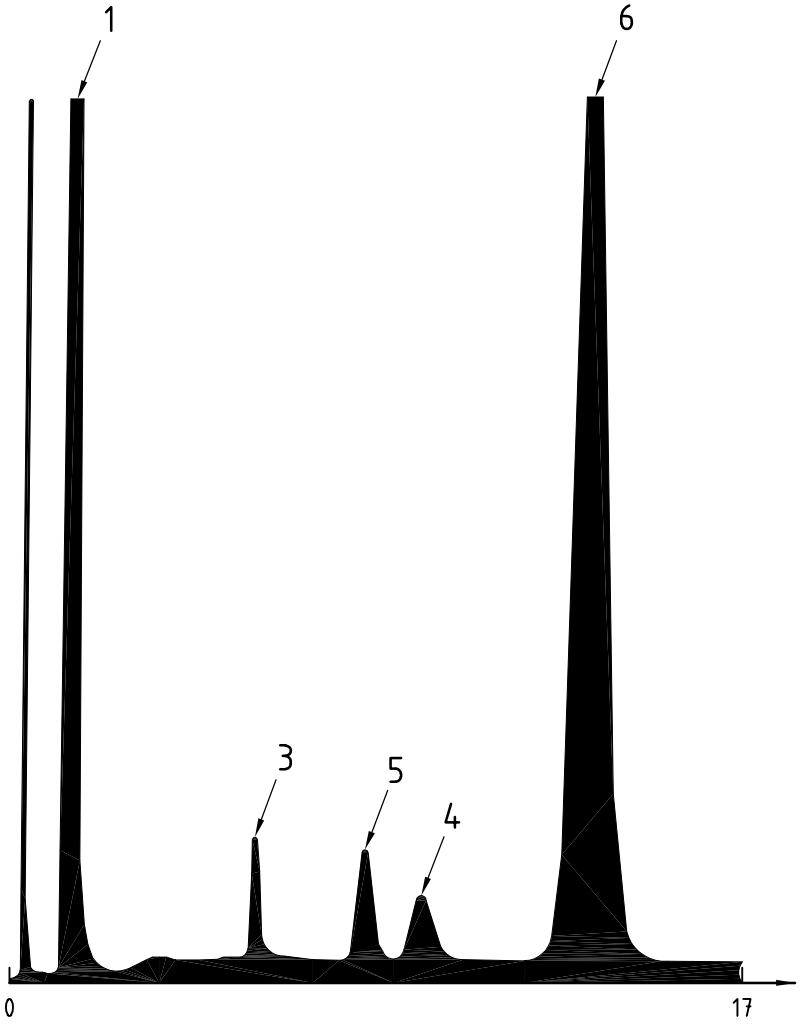
X time, min

1 H_2S (1,8 mg/m^3)

2 COS (~ 1 mg/m^3)

Figure G.7 — Chromatogram using Method 5

f) **Method 6** is a temperature-programmed Porapak QS method for measuring H_2S, COS, EtSH, TBM, MeSH and DES using a single column and a single sample injection. Figure G.8 is a chromatogram obtained using Method 6. Inject sample using the 10-port valve (V4) onto the Porapak QS pre-column in series with the Porapak QS analytical column (effectively a single Porapak QS column). Elute the H_2S and COS isothermally at 50 °C and then rapidly program the combined Porapak QS column to 150 °C at 35 °C/min. Then elute the mercaptans and sulfides isothermally at 150 °C. The analysis cycle is about 25 min (15 min analysis + 10 min cool-down).



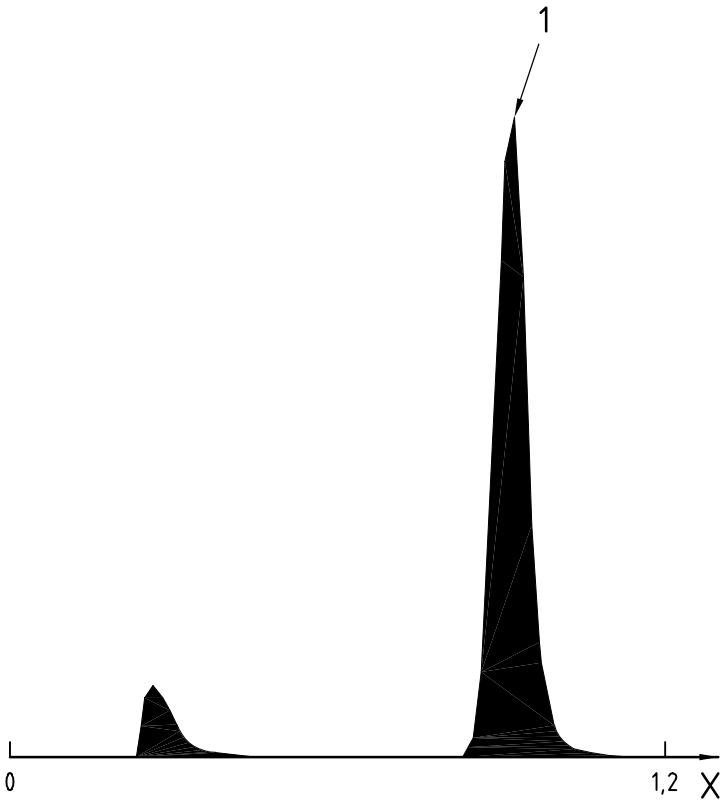
Key

X time, min

1 H_2S (12 mg/m^3)
2 COS (not determined)
3 EtSH (0,8 mg/m^3)
4 TBM (1,1 mg/m^3)
5 MeSH (1,0 mg/m^3)
6 DES (5,9 mg/m^3)

Figure G.8 — Chromatogram using Method 6

g) **Method 7** is a speeded-up version of Method 5. It is used for rapid H_2S analysis. Figure G.9 is a chromatogram obtained using Method 7. Speed up the method by increasing the carrier gas pressure from 336 kPa to 470 kPa, and by increasing the column temperature from 50 °C to 70 °C. Under these conditions, the hydrogen sulfide analysis cycle is about 1,2 minutes.



Key

X time, min

1 H_2S (3,4 mg/m^3)

Figure G.9 — Chromatogram using Method 7

G.4 Calculation

The relationship between the FPD response and the sulfur concentration is given by

$$A = k\,C^n \tag{G.1}$$

where

A is the signal of the component peak;

k is a constant;

C is the mass concentration;

n is the exponent.

Equation (G.1) can be rearranged to

$$\lg A = \lg k + n \lg C \tag{G.2}$$

For most accurate results, the exponent n must be determined with at least two standard gases containing the component of interest at 2 levels of concentration: the first at 20 % (C_1) of the full scale mass concentration and the second at 80 % (C_2). Then n is defined as

$$n = \frac{\lg \frac{A_1}{A_2}}{\lg \frac{C_1}{C_2}} \tag{G.3}$$

where

A_1 is the signal of the component peak at 20 % of the full scale;

A_2 is the signal of the component peak at 80 % of the full scale;

and

$$k = \frac{A_2}{{C_2}^n} \tag{G.4}$$

The n and k values can then be used to determine the mass concentration of the sample according to Equation (G.1).

The relationship between detector response and concentration is not linear (but the concentration is proportional to the square root of the area). Therefore, a calibration mixture shall be used in which the mass concentration of each component is close to the mass concentration of the same component in the sample to be analysed.

Annex H
(informative)

GC method using capillary column and SCD

H.1 Application

This method covers the determination of sulfur containing components in natural gas and similar gaseous mixtures at a mass concentration level of 0,5 mg/m^3 up to about 600 mg/m^3 by gas chromatography.

An application example for this working instruction is the quality control of natural gases, including the analysis of the following components:

— hydrogen sulfide (H_2S);

— carbonyl sulfide (COS);

— methane-, ethane-, *n*-propane-2-methylpropane-2-thiol (tert-butyl mercaptan) (MeSH, EtSH, *n*-PrSH TBM);

— diethylsulfide (DES);

— tetrahydrothiophene (THT, C_4H_8S).

H.2 Apparatus

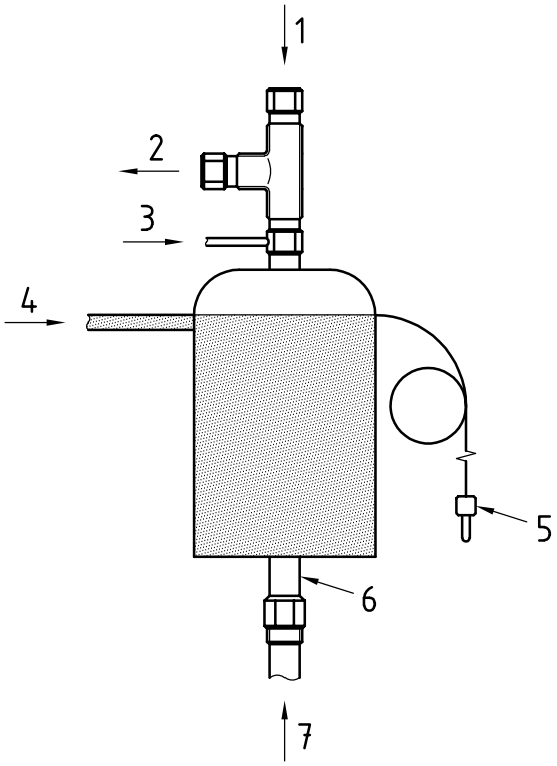
H.2.1 Gas chromatograph.

H.2.1.1 Capillary, fused-silica column, having a length of 25 m and an internal diameter of 0,53 mm, with packing of CP-PoraBOND Q[3)] of film thickness 10 µm.

H.2.1.2 Sulfur chemiluminescence detector (SCD). See Figure H.1.

H.2.2 Sample loop of 0,05 ml.

3) PoraBOND Q is an example of a product available commercially. This information is given for the convenience of users of this part of ISO 11933 and does not constitute an endorsement by ISO of this product.



Key

1 hydrogen inlet
2 outlet to reaction cell
3 air inlet
4 heater lead
5 thermocouple
6 Inconel tube (see Note)
7 column inlet

NOTE An Inconel tube is an example of a product available commercially. This information is given for the convenience of users of this part of ISO 11993 and does not constitute an endorsement by ISO of this product.

Figure H.1 — Arrangement of equipment

H.3 Procedure

H.3.1 Gas flows

Apply the following values.

— Helium: 85 kPa

— Gas flows at the controller

1) Hydrogen: 100 ml/min
2) Synthetic air: 40 ml/min
3) Oxygen: 8 ml/min

H.3.2 Temperatures

Apply the following temperatures.

— Oven: 50 °C for 5 min

— Heating rate: 10 °C / min

— Final temperature: 200 °C for 5 min

— Injector A: 115 °C

— Flameless interface: 800 °C (20 kPa to 33 kPa)

H.3.3 Detector

The SCD provides an efficient means of isolating and analyzing volatile sulfur compounds, producing a linear and equimolar response to sulfur compounds as follows.

— Sensitivity: $<$ 0,5 pg S/s

— Selectivity: $>$ 107 pg S/g C

— Linearity: $> 10^5$

The detector is not subject to quenching of sulfur compound response or interference from co-eluting compounds at the usual GC sampling volumes. The mechanism of operation of the SCD produces one response factor for sulfur, as opposed to other detectors where individual response factors for each analyte of interest must be determined.

The SCD is a sulfur-selective detector for gas (and supercritical fluid) chromatography. Its operation is based on the chemiluminescence (high-producing reaction) from the reaction of ozone with sulfur monoxide (SO) produced from combustion of the analyte:

$$\text{Sulfur compound (analyte)} + O_2 \rightarrow SO + H_2O + \text{other products}$$

$$SO + O_3 \rightarrow SO_2 + O_2 + h\nu\ (< 400)\ \text{(under normal reference conditions)}$$

A vacuum pump pulls the combustion products into a reaction cell at low pressure, where excess ozone is added. Light produced from the subsequent reaction is detected with a blue-sensitive photomultiplier tube and the signal is amplified for display or output to a data system.

The detector has an enclosed, dedicated hydrogen burner designed to enhance production of the SO intermediate. This burner is mounted in the detector port of the gas chromatograph. An interface controller provides temperature control and gas-flow regulation to operate the burner.

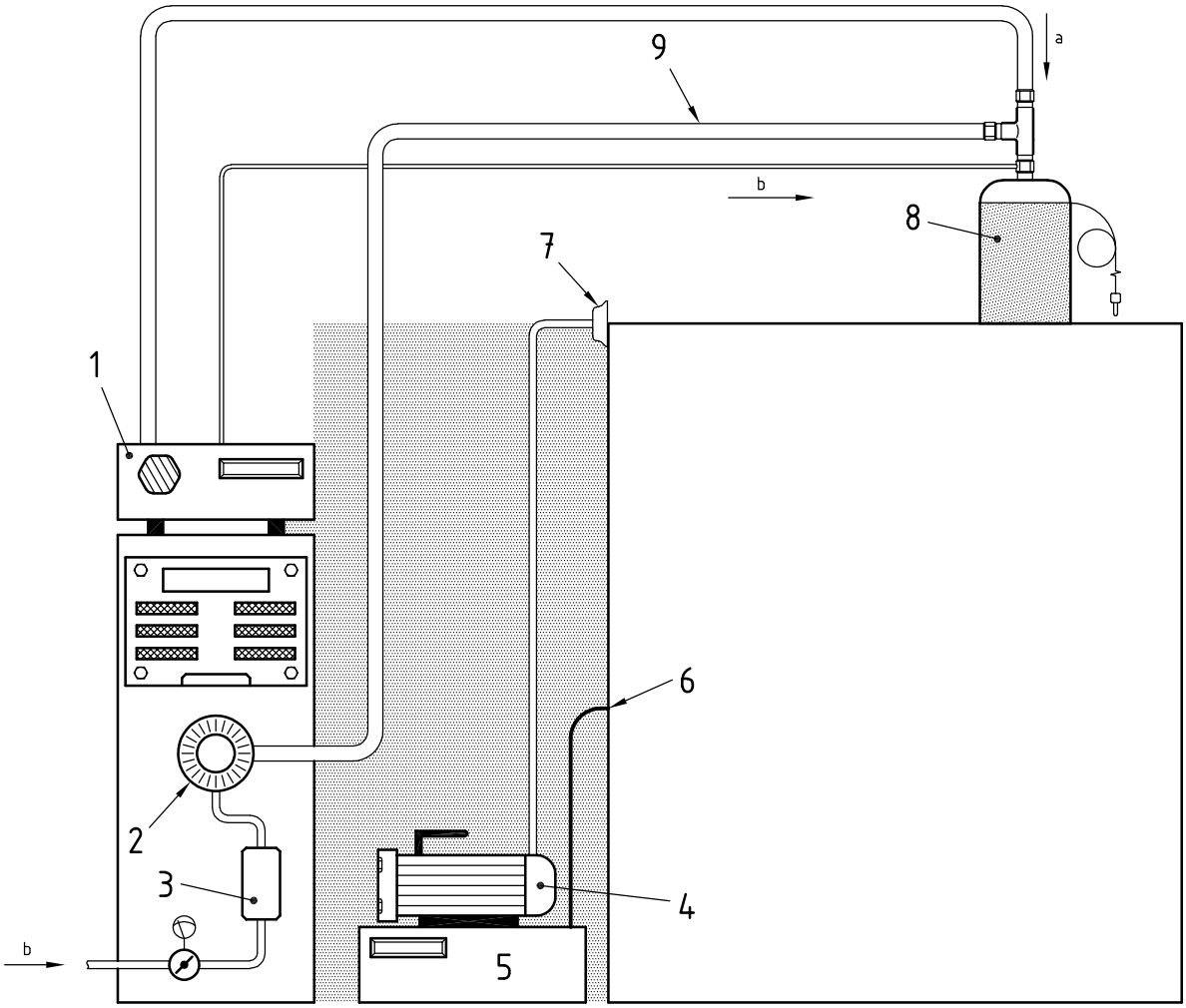
H.3.4 Interface controller

An interface controller provides all controls for the burner operation. Parameters monitored or regulated by the interface controller include burner temperature, hydrogen and air flow rates, and burner pressure.

H.3.5 Burner (see Figure H.2)

The burner consists of a tower assembly, which contains a furnace element, thermocouple, and Inconel combustion tube housing. Conversion of sulfur containing compounds to SO occurs within the ceramic reaction chamber housed in the burner assembly. The chromatographic column is routed into the bottom of the combustion zone and is attached to the stainless burner with a Hewlett-Packard[4)] connection for capillary columns.

4) Hewlett Packard® is the trade name of a product supplied by Hewlett Packard. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.



a) SCD **b) Sample inlet system** **c) Gas chromatograph**

Key

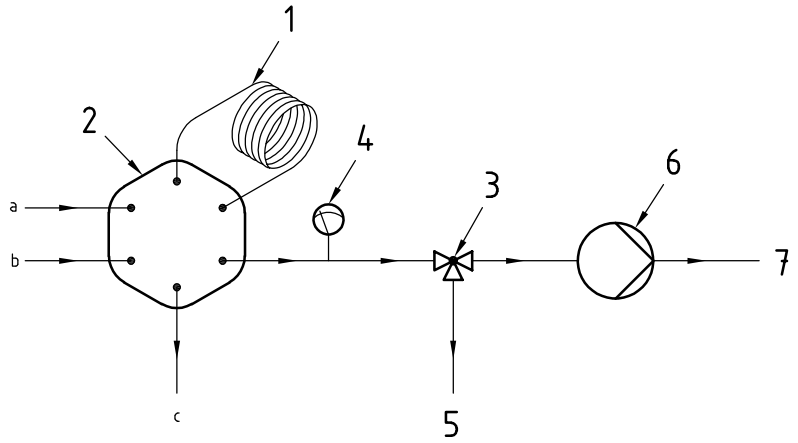
1 interface controller
2 reaction cell
3 ozone generator
4 vacuum pump mini A
5 vacuum controller
6 sample
7 sample inlet/vent
8 burner
9 transfer line

a Hydrogen.
b Air.

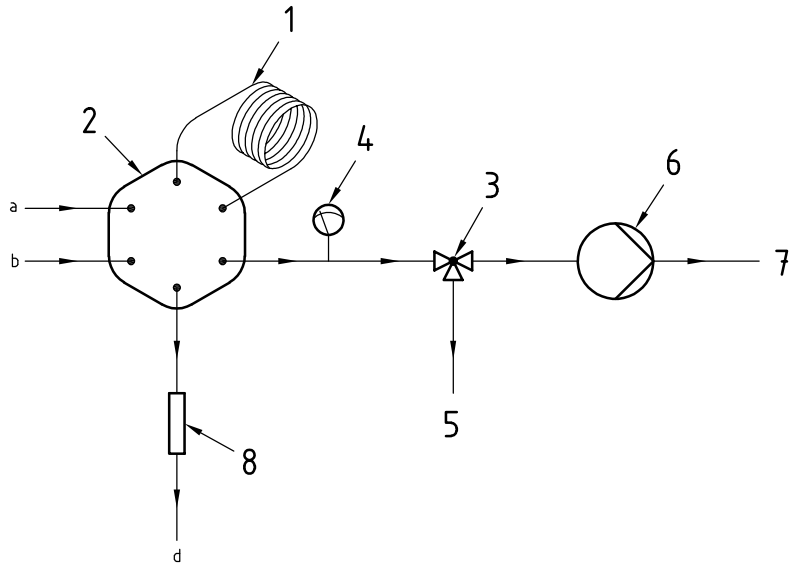
Figure H.2 — Burner

H.3.6 Sample injection device

See Figure H.3.



a) Direct interface at column



b) Split/splitless injection

Key

1 sample loop
2 6-port valve
3 3-way valve
4 pressure controller
5 vent 1
6 vacuum pump
7 vent 2
8 split/splitless injector

a Carrier in.
b Sample in.
c Direct interface to column.
d To column.

Figure H.3 — Sample injection device

H.3.7 Vacuum Pump

An oil-sealed vacuum pump is used to produce an operating pressure of between 0,3 kPa and 1,33 kPa in the reaction cell. The vacuum pump serves the SCD for the purposes of

— collection and transfer of the combustion gases from the burner to the reaction cell,

— transfer of ozone from the ozone generator to the reaction cell, and

— reduction of non-radioactive collisional quenching of the emitting species (SO_2) in the chemiluminescent reaction cell.

H.4 Elution times

These shall be the following.

— H_2S: 0,5 min

— COS: 0,9 min

— MeSH: 3,5 min

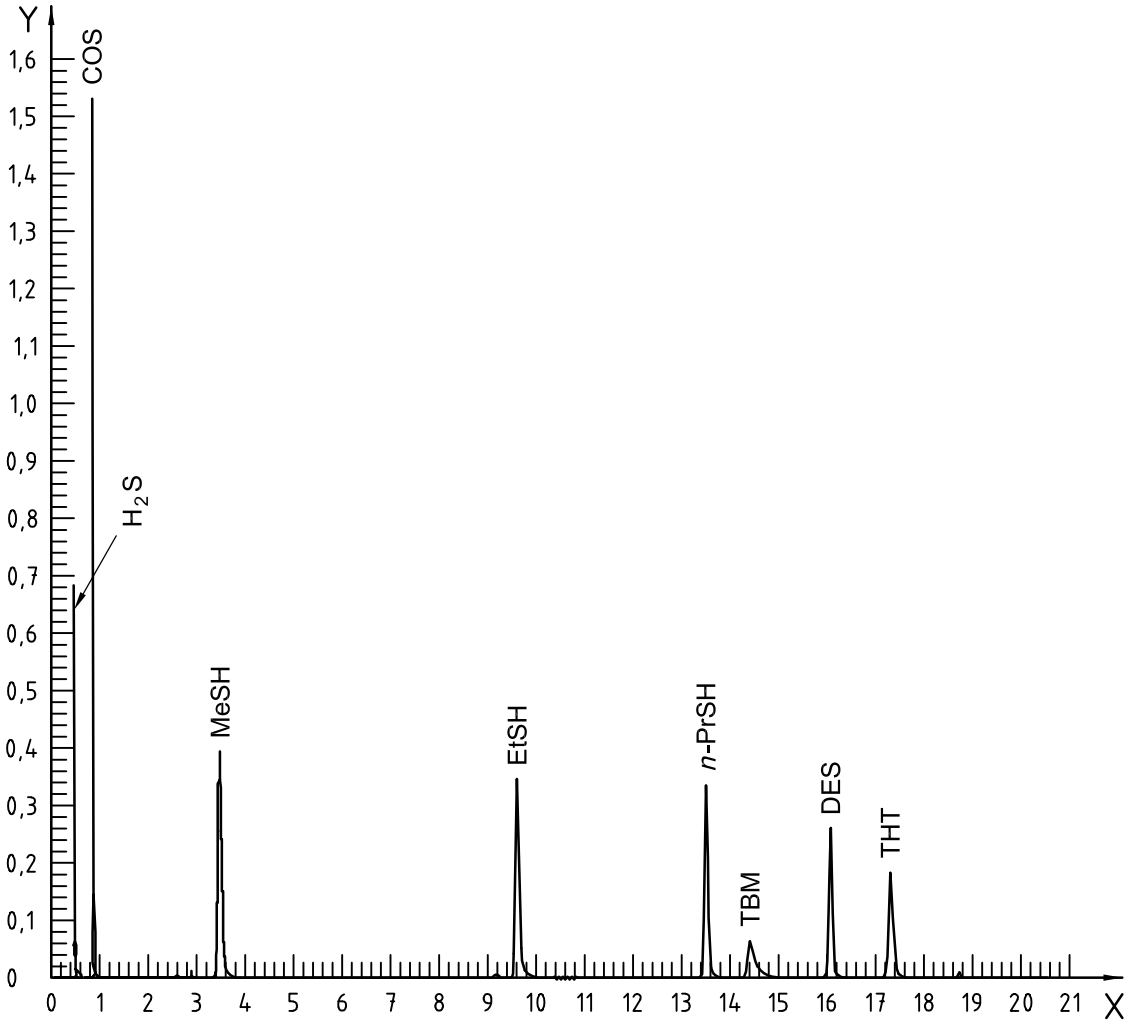
— EtSH: 9,5 min

— *n*-PrSH: 13,4 min

— TBM: 14,5 min

— DES: 16,1 min

— THT: 17,3 min



Key

X time, min

Y response ($\times 10^6$)

Figure H.4 — Chromatogram of Mixture 2 (COS, MeSH, EtSH, TBM, DES, THT in methane)

Annex I
(informative)

GC method using capillary column and PFPD

I.1 Application

The method is applicable to the following compounds:

— hydrogen sulfide (H_2S)

— carbonyl sulfide (COS)

— methane-, ethane-, 2-methylpropane-2-thiol (tert-butyl mercaptan) (MeSH, EtSH, TBM)

— diethyl sulfide (DES)

— tetrahydrothiophene (THT, C_4H_8S)

It is applicable for the determination of other mercaptans and sulfides but it could be necessary to adapt the operative procedures.

NOTE For the COS measurement in natural gas, with the conditions described below, there could be some interferences due to the quenching effect of propane.

I.2 Apparatus

I.2.1 Chromatograph, equipped with a specific detector and consisting of three parts, as follows.

I.2.1.1 Injection system, consisting of an electrical 10 port valve with a 250 µl inox loop.

I.2.1.2 Column of fused silica, 50 m in length and with an internal diameter of 0,53 mm, with CP-Sil 5 CB packing with a film thickness of 5 µm.

I.2.2 Detector

The detector used is a PFPD (pulsed flame photometric detector), based on a novel and patented approach and with a design consisting of an ignition source and combustible gas flow that is insufficient to sustain a continuous flame.

In operation, the ignited flame propagates through the detector, combusts the sample, then self terminates after the combustible mixture is consumed, creating a pulse of light emission. Sulfur, nitrogen and other heteroatoms are uniquely characterized by element-specific time-delayed radiation, exhibited after the termination of the pulsed flame. The C-H emission is very quick: $OH^* + C_2 \rightarrow CH^* + CO$. While those relative to the sulfur compounds arrive later and continue longer: $H + H + S_2 \rightarrow S_2^* + H_2$ and/or $S + S \rightarrow S_2^*$.

Using special electronics and appropriate band-pass filter, the signal is observed only during the emission of the element of interest, providing optimal selectivity.

The response of this detector to sulfur compounds is not quenched by hydrocarbons as is the normal FPD.

I.3 Procedure

I.3.1 Preparation of the apparatus

I.3.1.1 Carrier gas

This shall be helium (at least 99,995 %) at a pressure of approx. 4×10^5 Pa (4 bar) and a flow rate of 10 ml/min at 293 K (20 °C).

I.3.1.2 Injector

Apply the following conditions.

— Temperature: room temperature

— Purge time before first injection: 30 min

I.3.1.3 Detector

Apply the following conditions.

— Temperature: 150 °C

— Hydrogen flow rate: 10 ml/min

— Air 1 flow rate: 34 ml/min

— Air 2 flow rate: 10 ml/min

I.3.1.4 Column

a) Mixture 1

To separate H_2S and COS (1)

— Temperature: 35 °C isotherm

b) Mixture 2

All the other compounds

— Initial temperature: 40 °C for 3 min

— Heating rate: 15 °C/min

— Final temperature: 150°C

I.3.2 Analysis

The order and elution time for the constituents are

a) **Mixture 1**

— H_2S: 1,9 min

— COS: 2,0 min

b) **Mixture 2**

— MeSH: 2,8 min

— EtSH: 4,3 min

— TBM: 6,3 min

— DES: 8,4 min

— THT: 10,2 min

I.3.3 Calibration

Carry out external calibration.

I.4 Calculation

The relationship between the PFPD response and the sulfur concentration is given by

$$A = k\,C^{n} \tag{I.1}$$

where

A is the signal of the component peak;

k is a constant;

C is the mass concentration;

n is the exponent.

Equation (I.1) can be rearranged to

$$\lg A = \lg k + n \lg C \tag{I.2}$$

For most accurate results, the exponent n must be determined with at least two standard gases containing the component of interest at 2 levels of concentration: the first at 20 % (C_1) of the full scale mass concentration and the second at 80 % (C_2). Then n is defined as

$$n = \frac{\lg \dfrac{A_1}{A_2}}{\lg \dfrac{C_1}{C_2}} \tag{I.3}$$

where

A_1 is the signal of the component peak at 20 % of the full scale;

A_2 is the signal of the component peak at 80 % of the full scale.

and

$$k = \frac{A_2}{{C_2}^{n}} \tag{I.4}$$

The n and k values can then be used to determine the mass concentration of the sample according to Equation (I.1).

The relationship between detector response and concentration is not linear (but the concentration is proportional to the square root of the area). Therefore, a calibration mixture shall be used in which the mass concentration of each component is close to the mass concentration of the same component in the sample to be analysed.

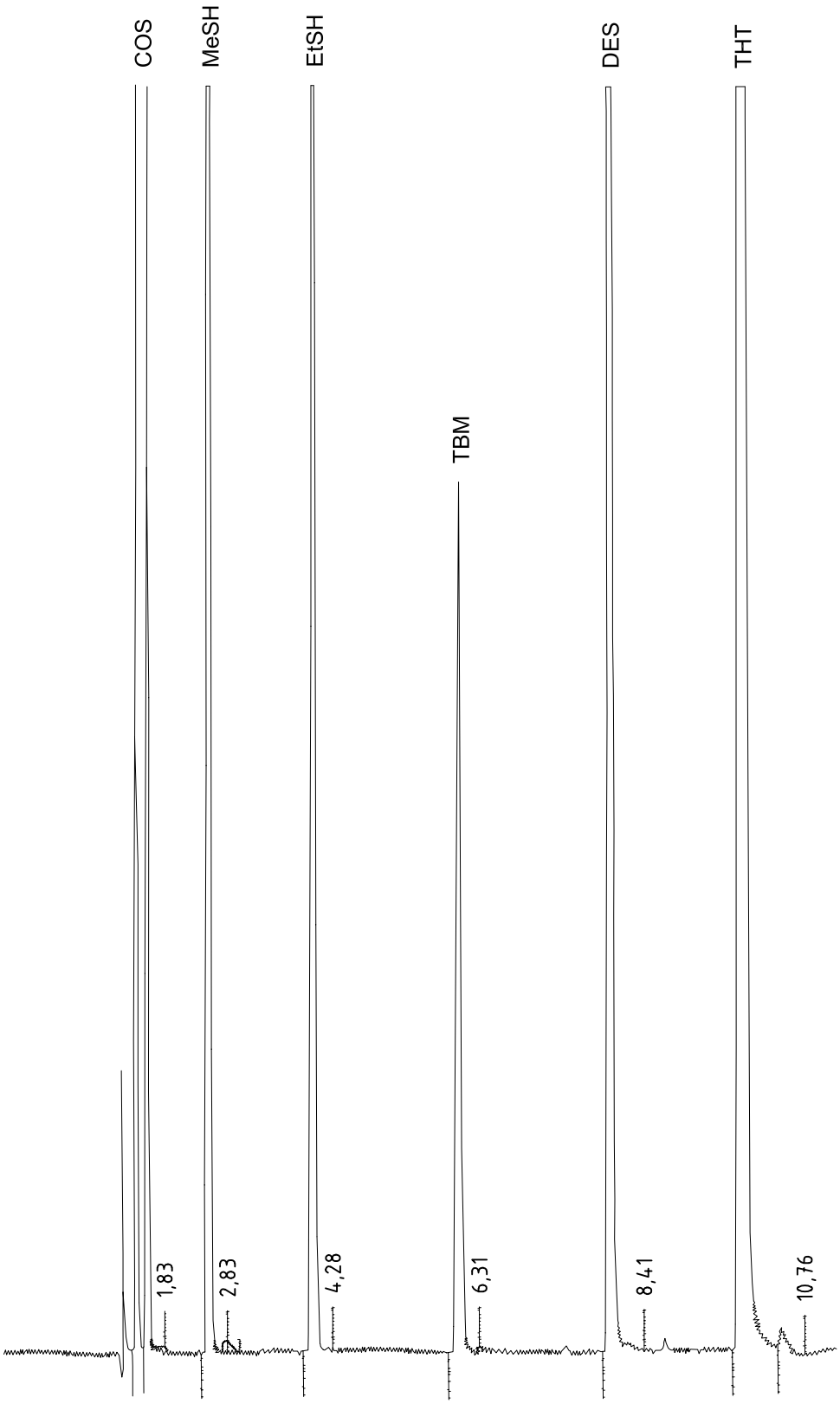


Figure I.1 — Chromatogram of mixture 2 (COS, MeSH, EtSH, TBM, DES, THT in methane)

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