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Natural gas — Determination of sulfur compounds —

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

Gaz naturel — Détermination des composés soufrés —

Partie 3 : Détermination du sulfure d'hydrogène, des thiols et du sulfure de carbonyle par potentiométrie

Reference number
ISO 6326-3 : 1989 (E)

Foreword

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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. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 6326-3 was prepared by Technical Committee ISO/TC 158, *Analysis of gases.*

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 sulfur compounds*

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

— *Part 4: Determination of individual sulfur compounds by gas chromatography with a flame photometric detector*

— *Part 5: Lingener combustion method*

International Organization for Standardization
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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*.

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Natural gas — Determination of sulfur compounds —

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

1 Scope

This part of ISO 6326 specifies a potentiometric method for the determination of hydrogen sulfide, mercaptan sulfur, and carbonyl sulfide sulfur in natural gas in the concentration range equal to or above 1 mg/m^3. The gas must be free of dust, mist, oxygen, hydrogen cyanide and carbon disulfide. The hydrogen sulfide/mercaptan sulfur ratio and also the mercaptan sulfur/hydrogen sulfide ratio should not exceed 50 : 1.

The method is not recommended for gases containing more than approximately 1,5 % (V/V) carbon dioxide.

NOTE — In all parts of ISO 6326, 1 m^3 of gas is expressed at normal conditions (0 °C; 101,325 kPa).

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 6326. At the time of publication, the editions indicated were 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 editions of the standards listed below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1 : 1984, *Laboratory glassware — Burettes — Part 1 : General requirements.*

ISO 648 : 1977, *Laboratory glassware — One-mark pipettes.*

ISO 1042 : 1983, *Laboratory glassware — One-mark volumetric flasks.*

3 Principle

Hydrogen sulfide and mercaptans are absorbed in a 35 % (m/m) aqueous potassium hydroxide solution and carbonyl sulfide in a 5 % (m/m) ethanoholic monoethanolamine solution. The solutions are titrated potentiometrically using silver nitrate solutions with a silver/silver sulfide electrode system to indicate the end point.

4 Reagents and materials

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Potassium hydroxide, solution.

Dissolve 35 g of potassium hydroxide (KOH) in 65 g of water.

NOTE — In order to prevent interference by heavy metal ions, 0,5 g of a mixture of polyaminoacetic acids is added for each 50 ml of absorption solution to inactivate the heavy metal ions.

The mixture consists of equal parts of

the pentasodium salt of diethylenetriamine pentaacetic acid (Na_5DTPA);

the trisodium salt of *N*-hydroxyethylenediamine triacetic acid (Na_3HEDTA);

the sodium salt of *N*,*N*-di(2-hydroxyethyl-glycin) (NaDHEG);

the tetrasodium salt of ethylenediamine tetraacetic acid (Na_4EDTA).

4.2 Monoethanolamine, solution.

Dissolve 5 g of monoethanolamine (C_2H_7ON) in 95 g of ethanol.

4.3 Nitrogen, purity better than 99,95 %, oxygen-free, under pressure.

4.4 Silver nitrate, standard volumetric solution, $c(AgNO_3) \approx 0,01$ mol/l.

For the preparation of the silver nitrate solution use boiled distilled water, cooled to 20 °C while bubbling with nitrogen (4.3), to remove all traces of oxygen.

Dissolve about 1,7 g of silver nitrate in 200 ml of water in the 1 000 ml one-mark volumetric flask (5.6) and make up to the mark with water. Standardize the solution with hydrochloric acid [$c(HCl) = 0,01$ mol/l].

4.5 Ammonium hydroxide solution ($\varrho_{20\,°C} = 0,90$ g/ml).

4.6 Electrolyte solution.

Mix 1 000 ml of methanol and 25 ml of ammonium hydroxide solution (4.5).

4.7 Cotton-wool, for the removal of dust.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Test apparatus, (see figure 1), consisting of three washing bottles (high-speed absorbers of any suitable design), maximum pore diameter 90 µm to 150 µm; 1 washing bottle for the removal of dust, if required; gas meter, wet design, tolerance 0,1 litre, with thermometer and water manometer. The thermometer shall have a measuring range of 0 °C to at least 30 °C. The scale intervals shall be not less than 0,5 °C.

The connections between the three washing bottles shall be glass to glass sealed by fluorelastomer tubing.

NOTE — For low levels of sulfur compounds, butt connections and stop cocks with polytetrafluoroethylene plugs instead of the screw clamps are recommended.

5.2 One-mark pipette, of capacity 10 ml, complying with ISO 648.

5.3 Microburette, of capacity 10 ml, complying with ISO 385-1.

5.4 Beaker, of capacity 300 ml.

5.5 Measuring cylinder, of capacity 50 ml.

5.6 One-mark volumetric flask, of capacity 1 000 ml, complying with ISO 1042.

5.7 High-resistance voltmeter, range 1 000 mV, accuracy better than ± 5 mV. (An automatic titrimeter may be used, providing that it meets the above specification.)

5.8 Silver/silver sulfide measuring electrode

NOTE — Ion-selective silver/silver sulfide crystal membrane electrodes are commercially available and allow faster and more precise titration, especially at low sulfur concentrations. If such an electrode is not available, a conventional silver/silver sulfide electrode may be prepared according to the following procedure.

Prepare a solution of sodium sulfide and sodium hydroxide by dissolving 1,2 g of sodium sulfide nonahydrate ($Na_2S,9H_2O$) and 40 g of sodium hydroxide in 1 litre of water.

Clean the silver metal of the electrode with fine abrasive paper and immerse it in 100 ml of the sodium sulfide/sodium hydroxide solution, stir the solution and add 10 ml of the silver nitrate solution (4.4) over a period of 10 min to 15 min. Remove the electrode from the solution, wash it with water and wipe it lightly with a clean cloth. The coating should last for several weeks.

Before use, soak the electrode for at least 5 min in 100 ml of the electrolytic solution (4.6) to which 0,5 ml of silver nitrate solution (4.4) has been added. Store the electrode in this solution.

5.9 Silver/silver chloride reference electrode.

5.10 Electric stirrer.

6 Sampling

On-line sampling is recommended. In the case where indirect sampling is indispensable, use sampling cylinders in accordance with clause 3 of ISO 6326-1 : 1989.

7 Procedure

7.1 Preliminary operations

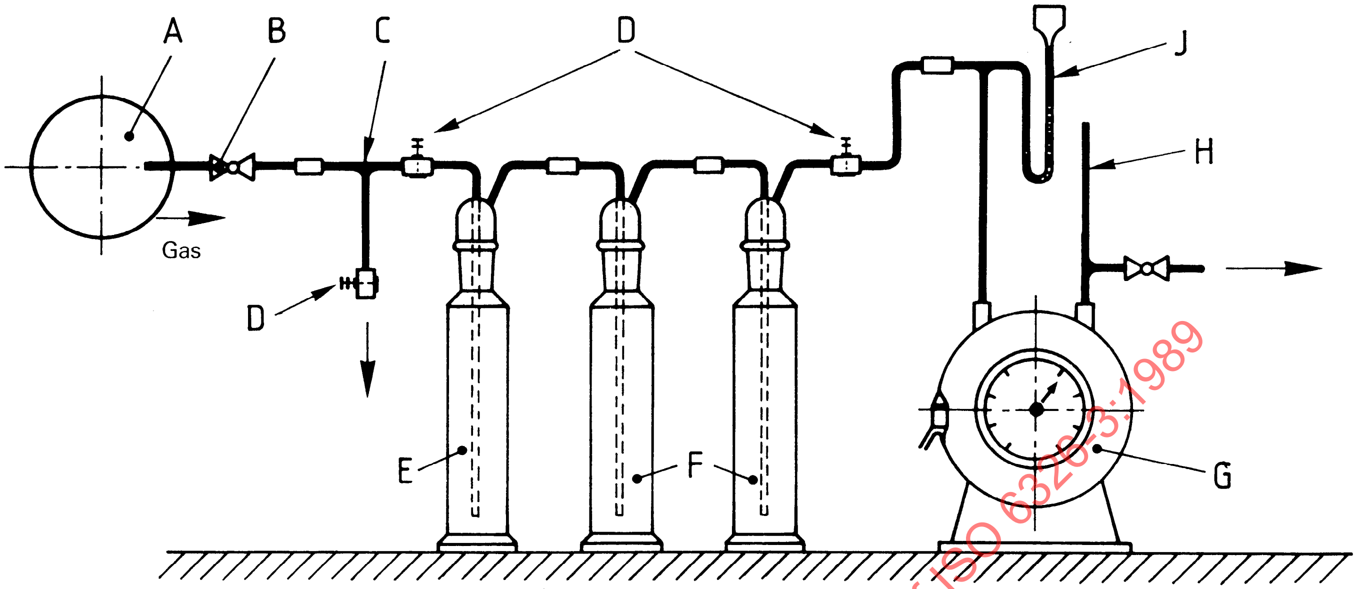
Assemble the absorbers in series, as shown in figure 1.

Place 50 ml of potassium hydroxide solution (4.1) in the washing bottle (E), and 50 ml of monoethanolamine solution (4.2) in each of the two washing bottles (F). In order to remove the oxygen dissolved in the absorption solutions, purge the assembly with nitrogen (4.3) for a period of 5 min to 10 min, at a rate of 1 l/min to 2 l/min.

Transfer the washing bottles, closed hermetically with screw-clamps (D), to the sampling point and assemble the testing apparatus as shown in figure 1. If required, connect an additional washing bottle filled with cotton-wool (4.7) between the sampling cock (B) and the T-piece (C) to intercept any solid particles.

7.2 Absorption (see figure 1)

Flush the sampling line and the T-piece (C) with gas. Open the screw-clamps (D) at the inlet and outlet of the washing bottles (E and F) and record the initial reading of the gas meter (G).



A	Gas line
B	Sampling valve
C	T-piece
D	Screw-clamp
E	Washing bottle for potassium hydroxide solution
F	Washing bottles for monoethanolamine solution
G	Gas meter
H	Thermometer
J	Water manometer

Figure 1 — Test apparatus

The gas is passed through the absorption solutions at a flow rate of 120 l/h ± 20 l/h. Read the temperature and pressure of the gas and the atmospheric pressure during the absorption period. The amount of gas depends on the content of sulfur compounds; 100 litres to 200 litres are sufficient in most cases.

Close the sampling valve (B) and read the amount of gas passed through the solutions on the gas meter (G). By the free end of the T-piece, pass 10 litres of nitrogen (4.3) through the washing bottles to transfer the dissolved carbonyl sulfide from the potassium hydroxide into the monoethanolamine solution. Close the washing bottles (E and F) hermetically and titrate the solutions containing the absorbed sulfur compounds immediately.

7.3 Potentiometric titration

7.3.1 Determination of hydrogen sulfide and mercaptan sulfur

Flush the 300 ml beaker (5.4) with nitrogen (4.3). Quantitatively transfer the contents of the washing bottle (E) into the beaker and dilute with approximately 200 ml boiled distilled water, cooled to 20 °C. While bubbling with nitrogen (4.3), add 2 ml of concentrated ammonium hydroxide solution (4.5) using the pipette (5.2).

CAUTION — Ammonia must not be added after the titration has commenced because of possible formation of explosive compounds.

The dilution of the absorption solution is necessary to reach a fast response of the voltmeter (5.7).

Immerse the electrodes (5.8 and 5.9) in this mixture. Start a nitrogen purge of the liquid surface and continue this throughout the titration. Stir the solution with the electric stirrer (5.10). Start titration as soon as a constant voltage is attained (initial voltage). This condition is fulfilled if the voltage varies by less than 5 mV/min. For high levels of sulfur compounds it is recommended to titrate an aliquot part of the diluted absorption solution while adding an appropriate amount of ammonium hydroxide solution (4.5).

Carry out the titration with the standard volumetric silver nitrate solution (4.4), initially in steps of 0,5 ml. The tip of the microburette shall be immersed about 20 mm in the solution during the entire titration process. Measure the voltage after adding each 0,5 ml of silver nitrate solution. Resume the titration after a constant voltage is attained. 5 min to 10 min may elapse before an unchanging potential is attained.

If, after each addition of silver nitrate solution, the voltage varies by more than 10 mV, reduce the volumes of silver nitrate solution added from 0,5 ml to 0,1 ml and from 0,1 ml to

0,05 ml. Continue the titration until the change of the voltage is less than 5 mV for 0,1 ml of solution and the voltage exceeds + 200 mV. Then record the voltage and microburette reading.

NOTE — The voltage depends on the electrode combination. The values given should be regarded as approximative values.

7.3.2 Determination of carbonyl sulfide sulfur

Quantitatively transfer the absorption solutions in the washing bottles (F) to the beaker (5.4) and add 50 ml of the electrolyte solution (4.6). Carry out the titration as described in 7.3.1. The initial voltage may be − 350 mV. The titration should be continued to a final voltage of + 100 mV. Since the intermediate voltages are attained very slowly, several minutes will be required, especially at the end of the titration, after each addition of the silver nitrate solution (4.4).

CAUTION — To avoid accidents due to the formation of highly explosive silver fulminate, the solution must be disposed of immediately after titration is completed.

NOTE — The voltage depends on the electrode combination. The values given should be regarded as approximative values.

7.3.3 Graphic presentation of titration curves

Plot the volumes of standard volumetric silver nitrate solutions used against the voltages measured, on a coordinate system. Determine the end points for hydrogen sulfide (approximately − 320 mV) and for mercaptan sulfur (approximately + 100 mV), on the titration curve obtained according to 7.3.1 and record the corresponding volume of silver nitrate solution used. The potentials may vary with different makes of instruments.

Figure 2 shows a typical titration curve.

Titration in accordance with 7.3.2 should show a similar curve with only one end point.

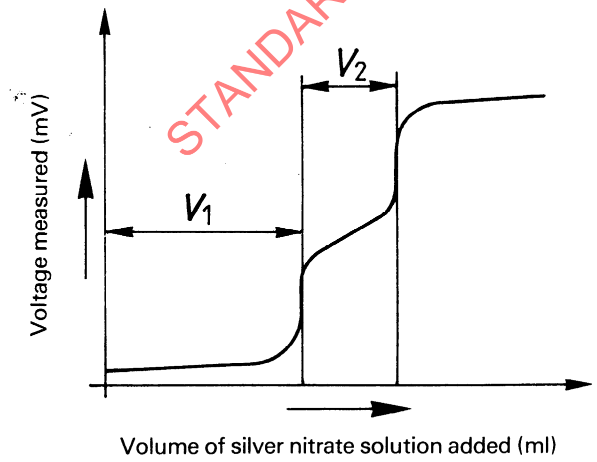


Figure 2 — Example of a titration curve (see 7.3.3)

8 Expression of results

8.1 Method of calculation

The mass concentration of hydrogen sulfide $\varrho(H_2S)$, expressed in milligrams per cubic metre, is given by the equation

$$\varrho(\mathrm{H_2S}) = \frac{17\,cV_1}{V_\mathrm{n}}$$

The mass concentration of mercaptan sulfur ϱ(S-RSH), expressed in milligrams per cubic metre, is given by the equation

$$\varrho(\mathrm{S\text{-}RSH}) = \frac{32\,cV_2}{V_\mathrm{n}}$$

The mass concentration of carbonyl sulfide sulfur ϱ(S-COS), expressed in milligrams per cubic metre, is given by the equation

$$\varrho(\mathrm{S\text{-}COS}) = \frac{16\,cV_3}{V_\mathrm{n}}$$

where

c is the actual concentration, in moles per litre, of standard volumetric silver nitrate solution (4.4) used [$c(AgNO_3) \approx$ 0,01 mol/l];

V_1 is the volume, in millilitres, of standard volumetric silver nitrate solution (4.4) used in titrating to the first inflexion in the curve (corresponding to the mass concentration of hydrogen sulfide) (see figure 2);

V_2 is the volume, in millilitres, of standard volumetric silver nitrate solution (4.4) added in titrating between the first and second inflexions in the curve (corresponding to the mass concentration of mercaptan sulfur) (see figure 2);

V_3 is the volume, in millilitres, of standard volumetric silver nitrate solution (4.4) added to reach the end point (corresponding to the mass concentration of carbonyl sulfide sulfur), in accordance with 7.3.2;

V_n is the total volume, in cubic metres, of dry gas analysed at normal conditions:

$$V_\mathrm{n} = \frac{V T_\mathrm{n} (p_\mathrm{amb} + p_\mathrm{e} - p_\mathrm{D})}{p_\mathrm{n} T}$$

V is the volume of the gas sample measured according to 7.2 at temperature T (kelvins) and pressure p (kilopascals):

$$p = p_\mathrm{amb} + p_\mathrm{e} - p_\mathrm{D}$$

T_n is the thermodynamic temperature, in kelvins, at normal conditions (273,15 K);

T is the thermodynamic temperature, in kelvins, of the gas sample;

p_n is the pressure, in kilopascals, at normal conditions (101,325 kPa);

p_{amb} is the atmospheric pressure, in kilopascals, measured during gas sampling;

p_e is the excess pressure, in kilopascals, measured with the water manometer during gas sampling;

p_D is the partial pressure of water vapour, in kilopascals, in the gas meter at T (kelvins).

Round the results to the nearest 0,1 mg/m³.

8.2 Precision

The precision of the method, as obtained by statistical examination of interlaboratory test results, is as follows.

8.2.1 Repeatability

The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test gas would, in the long run, in the normal and correct operation of the test method, exceed the values given in table 1 in only one case out of twenty.

8.2.2 Reproducibility

The difference between two single and independent results, obtained by different operators working in different laboratories on identical test gases would, in the long run, in the normal and correct operation of the test method, exceed the values given in table 1 in only one case out of twenty.

9 Test report

The test report shall include the following information:

a) a reference to this part of ISO 6326;

b) all information necessary for the complete identification of the sample (e.g. type and identification of the gas tested and the date of sampling);

c) the sampling method used;

d) the results and the method of calculation used;

e) details of any deviation from the procedure specified in this part of ISO 6326 or any circumstance that may have influenced the results.

Table 1 — Precision data

Concentration range mg/m^3	Repeatability %	Reproducibility %
$\varrho(H_2S)$: 1 to 10 ϱ(S-RSH) : 1 to 20	15	20
ϱ(S-COS) : 1 to 30	10	15