International Standard ISO 6569

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Natural gas — Rapid analysis by gas chromatography

Gaz naturel — Analyse rapide par chromatographie en phase gazeuse

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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 6569 was developed by Technical Committee ISO/TC 158, *Analysis of gases*, and was circulated to the member bodies in May 1980.

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

Australia
Belgium
Brazil
Bulgaria
Czechoslovakia
Egypt, Arab Rep. of
France
Germany, F.R.
Mexico
Netherlands
Philippines
Poland
Romania
South Africa, Rep. of
Spain
USSR

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

India
United Kingdom

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Natural gas — Rapid analysis by gas chromatography

0 Introduction

This International Standard describes a simple method for the rapid analysis of dry natural gas. The method employs an isothermal gas chromatograph fitted with a thermal conductivity detector. The detector and associated electronic equipment must have a rapid response; a response time not greater than 0,1 s is suitable.

The method provides for the measurement of nitrogen, carbon dioxide, hydrocarbons having up to four carbon atoms (C_1 to C_4) and hydrogen sulphide. It is primarily intended for the preliminary examination of samples during exploration and for control purposes before treatment.

ISO 6568[1] specifies an alternative simple method which enables the determination of nitrogen, carbon dioxide and hydrocarbons having up to 5 carbon atoms (C_1 to C_5) in natural gas. More detailed methods for the analysis of natural gas will form the subjects of future International Standards.

1 Scope and field of application

This International Standard specifies a method for the rapid analysis of dry natural gas containing less than 1 % (molar) of hydrocarbons having five or more carbon atoms. It is applicable for the determination of :

- hydrocarbons having one to four carbon atoms;
- nitrogen;
- carbon dioxide;
- hydrogen sulphide.

The method does not distinguish between oxygen and nitrogen and contamination of the samples by air will give an apparently high value for the nitrogen content.

The method is generally applicable to test samples containing the elements and compounds given in table 1 in the ranges indicated.

Table 1

Element or compound	Range, % molar
Nitrogen (N_2)	1 to 20
Methane (CH_4)	> 75
Carbon dioxide (CO_2)	0 to 3
Ethane (C_2H_6)	0,5 to 10
Propane (C_3H_8)	0,1 to 5
Butanes (C_4H_{10})	0,1 to 1
Higher hydrocarbons	< 1 total
Hydrogen sulphide (H_2S)	0,1 to 5

2 References

ISO 6142, *Gas analysis — Preparation of calibration gas mixtures — Gravimetric method.*

ISO 6143, *Gas analysis — Determination of composition of calibration gas mixtures — Comparison method.*

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

3 Materials

3.1 Carrier gas.

- Nature : helium
- Purity : > 99,9 %

3.2 Calibration gas mixture.

The components of the mixture shall be 99 % pure or better (see 6.2.1), except methane which shall be 99,9 % pure.

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[1] ISO 6568, *Natural gas — Simple analysis by gas chromatography.*

4 Apparatus

4.1 Thermal conductivity gas chromatograph, comprising

4.1.1 Column oven, capable of operating at approximately 120 °C, and providing temperature control better than ± 0,2 °C during the analysis.

4.1.2 Pressure or **flow regulators,** to give suitable carrier gas flow rates.

4.1.3 Injection device.

- Type : by-pass injector (gas sampling valve), capable of injecting a sample of 0,5 ml.
- Material : stainless steel/PTFE.

4.1.4 Chromatography column

4.1.4.1 Tube

- Material : TS 60 stainless steel, seamless, annealed and degreased
- Length : 3 m (see note 2 to 4.1.4.2.1)
- Diameter : 2 mm internal diameter
  3,2 mm external diameter
- Form : appropriate to the chromatograph
- Radius : appropriate to the chromatograph

4.1.4.2 Packing

4.1.4.2.1 Materials

- Nature :
  - Porapak T
  - Porapak Q (see note 2)
- Particle size: 150 to 180 µm (100 to 80 mesh)

NOTES

1 Preliminary treatment overnight at 180 °C with flowing carrier gas will result in more stable baselines.

2 If water vapour interferes with the determination of butanes, a further section of column, 1 m long, packed with the Porapak Q may be added to the analytical column. This causes water to elute between propane and *iso*-butane.

4.1.4.2.2 Method of filling

Close the column outlet with a sintered disc or glass wool plug. Connect a reservoir containing rather more packing than is needed to fill the column to the inlet, and apply a pressure of 400 kPa of nitrogen to the reservoir. Any method of filling which leads to regular packing of the column may be used. When the column is full, turn off the supply of nitrogen and allow the pressure to fall by normal leakage before disconnecting the reservoir.

4.1.4.3 Performance

When operated under the recommended conditions, the separation between nitrogen and methane shall be such as to give a peak height/valley ratio of not less than 4 : 1 for 3 % molar nitrogen (N_2).

4.2 Detector, thermal conductivity type, capable of being separately heated.

If an amplifier is used, the response time of the assembly shall not be greater than 0,1 s.

4.3 Potentiometric recorder.

- Sensitivity : appropriate to the detector (usually 1 to 10 mV)
- Impedance : > 2 000 Ω
- Response time : not greater than 0,5 s.

4.4 Integrator (if used), range 0 to 1 V, capable of baseline tracking, and of measuring peak areas on a sloping baseline.

5 Procedure

5.1 Control of the apparatus

5.1.1 By-pass injector

The by-pass injector shall be at ambient temperature. If there is a separately heated injection zone which affects the temperature of the first part of the column, set this to 120 ± 10 °C.

5.1.2 Oven and column

5.1.2.1 Set the isothermal oven temperature to 120 ± 5 °C.

5.1.2.2 Set the carrier gas flow rate to 35 ml/min. This requires an inlet pressure of approximately 400 kPa.

5.1.3 Detector

5.1.3.1 Set the temperature to 150 ± 10 °C.

5.1.3.2 Set the bridge current or filament temperature to the maximum setting recommended by the manufacturer for the above conditions.

5.1.4 Recorder

Set the chart speed to a minimum of 1 cm/min.

5.1.5 Integrator

Set up the integrator, if used, in accordance with the manufacturer's instructions. Ensure that the integrator receives the largest signal commensurate with its dynamic range. Attenuate the recorder signal, if desired, independently of the integrator input.

5.2 Calibration

5.2.1 The calibration mixture should have a composition close to that of the sample; components shall be within 2 % actual or 50 % relative, whichever is the smaller, of the concentration in the sample. The calibration mixture shall be prepared by one of the methods specified in ISO 6142 (gravimetric method), ISO 6143 (comparison method) or ISO 6146 (manometric method).

5.2.2 To avoid the necessity of including hydrogen sulphide in the calibration gas mixture, measurements for H_2S may be made by applying the response coefficient relative to propane, which is 1,3.

5.2.3 Inject the calibration gas mixture (5.2.1), if possible, immediately before or immediately after each analysis. If analyses are being performed continuously, inject the standard mixture at least twice a day, once in the morning and once in the afternoon.

5.3 Determination

5.3.1 Inject the sample to be analysed, ensuring that it reaches conditions of ambient temperature and pressure in the loop before it is injected. Inject the appropriate calibration mixture under the same conditions.

5.3.2 Attenuate the signal of the recorder so that the components which are to be measured from the chromatogram have peak heights between 30 and 100 % full scale deflection or are recorded at the maximum sensitivity compatible with accurate baseline estimation.

5.4 Examination of the chromatogram

NOTE — The figure shows an example of a chromatogram.

5.4.1 The order of elution of components, and retention times relative to *n*-butane from the time of injection, are given in table 2. The retention time for butane is approximately 5 min.

Table 2

Component	Relative retention time
Nitrogen (N_2)	0,06
Methane (CH_4)	0,07
Carbon dioxide (CO_2)	0,12
Ethane (C_2H_6)	0,14
Hydrogen sulphide (H_2S)	0,25
Propane (C_3H_8)	0,35
iso-Butane (*i*-C_4H_{10})	0,83
n-Butane (*n*-C_4H_{10})	1,00

Water, if present, elutes between *iso*- and *n*-butane but can be distinguished from them (see note 2 to 4.1.4.2.1).

5.4.2 Measure the areas of the peaks due to components in the sample and in the calibration gas mixture. If a component has been measured at different attenuations in the sample and the calibration gas mixture, convert the measurements to the same attenuation.

6 Expression of results

6.1 Calculate the concentration of each component in the sample which is also present in the calibration gas mixture from the formula

$$C_i = E_i \left(\frac{A_i}{A_E} \right)$$

where

C_i is the concentration of substance i in the sample;

E_i is the concentration of substance i in the calibration gas mixture;

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

A_E is the area of peak i on the chromatogram of the calibration gas mixture.

6.2 Calculate the concentration of hydrogen sulphide in the sample from the formula

$$C_{H_2S} = E_{C_3} \left(\frac{A_{H_2S}}{A_{C_3}} \right) K_F$$

where

C_{H_2S} is the concentration of hydrogen sulphide in the sample;

E_{C_3} is the concentration of propane in the calibration gas mixture;

A_{H_2S} is the area of the hydrogen sulphide peak on the chromatogram of the sample;

A_{C_3} is the area of the propane peak on the chromatogram of the calibration gas mixture;

K_F is the response coefficient for hydrogen sulphide relative to propane.

6.3 The sum of the concentrations obtained shall be normalized to 100 %, even if all the components have not been analysed.

7 Precision

The repeatability of the method, expressed as relative standard deviation, is of the order of 1 % for methane, better than 1 % for other components in concentrations down to 1 % molar, and between 3 and 10 % for components in concentrations less than 1 % molar.

The reproducibility of the method has not been assessed.

8 Test report

The test report shall include the following information :

a) a reference to this International Standard;

b) identification of the sample;

c) the results;

d) any unusual features noted during the analysis;

e) any operations not included in this International Standard, or regarded as optional.

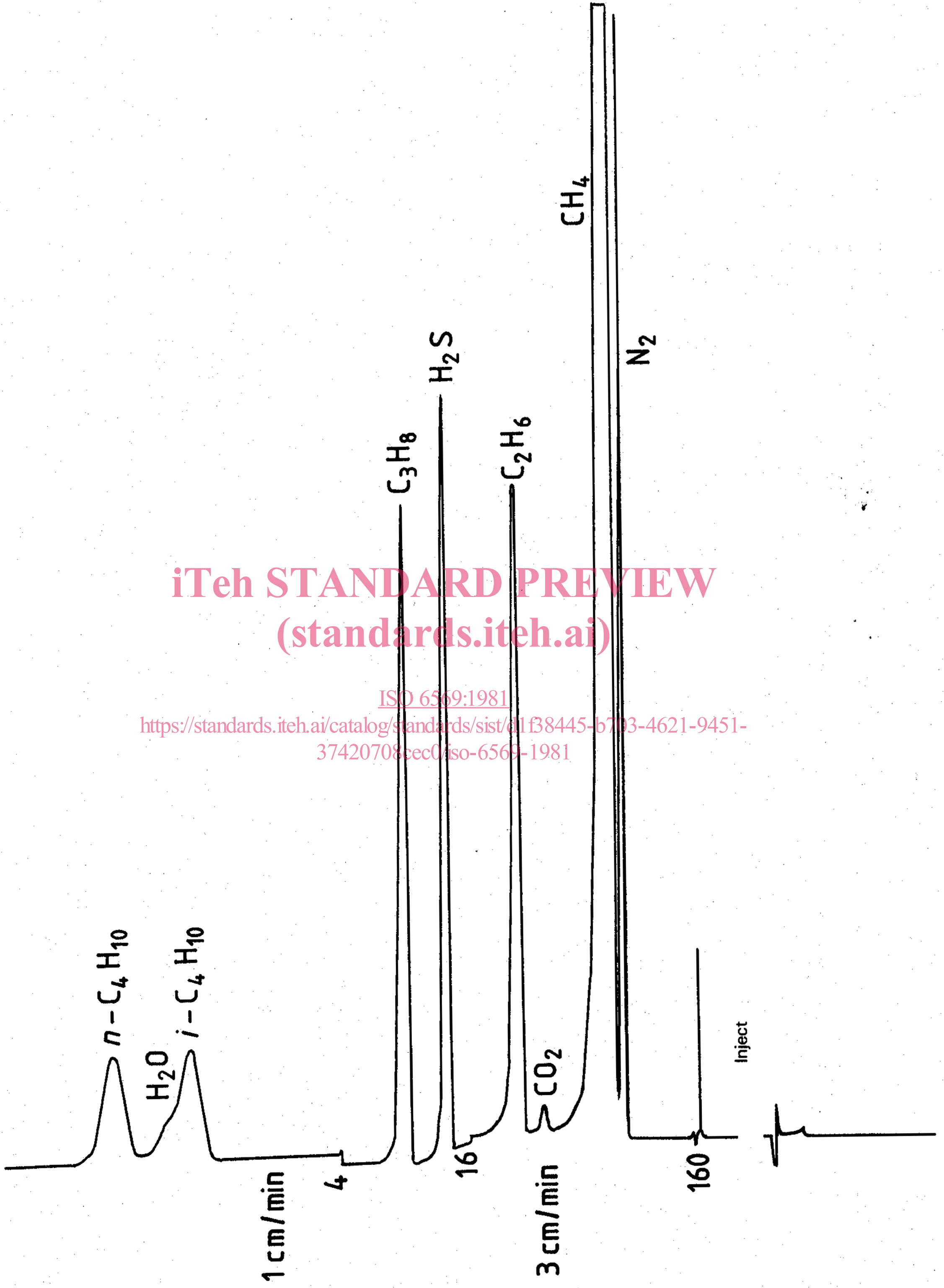

Figure — Example of chromatogram