International Standard 6568

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Natural gas — Simple analysis by gas chromatography

Gaz naturel — Analyse simple par chromatographie en phase gazeuse

First edition — 1981-09-01

UDC 665.612.3 : 543.544 **Ref. No. ISO 6568-1981 (E)**

Descriptors : gas analysis, natural gas, gas chromatographic analysis.

Price based on 4 pages

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 6568 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
France
Germany, F.R.
Italy
Mexico
Netherlands
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

Printed in Switzerland

INTERNATIONAL STANDARD **ISO 6568-1981 (E)**

Natural gas — Simple analysis by gas chromatography

0 Introduction

This International Standard describes a simple method for the analysis of natural gas. It can be used with any kind of gas chromatograph fitted with a thermal conductivity detector with filament, capable of isothermal operation, and with a single column.

The method allows determination of the contents of nitrogen, carbon dioxide and hydrocarbons containing one to five carbon atoms.

ISO 6569[1] specifies an alternative method of rapid analysis of natural gas (hydrocarbons up to butane). 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 analysis of natural gas containing less than 1 % molar of hydrocarbons containing more than 5 carbon atoms (generally called dry natural gas), at any point from extraction up to the distribution centre. It is applicable for the determination of :

- hydrocarbons having one to five carbon atoms[2];
- carbon dioxide;
- nitrogen[3].

For the purposes of this International Standard, the gas is assumed to be dehydrated or containing less than 2 % molar of water vapour, and containing no hydrogen sulphide, carbonyl sulphide or mercaptans in quantities that are measurable with the detector used.

2 Apparatus and materials

2.1 Chromatography column

2.1.1 Tube[4]

- Length : 9 m
- Diameter : 4 mm internal diameter
  6 mm external diameter
- Material : Copper or stainless steel for example

2.1.2 Packing[5]

- Mass : 80 to 100 g

2.1.2.1 Support

- Nature : Chromosorb P
- Particle size : 250 to 315 µm (60 to 48 mesh)
- Treatment : acid-washed

2.1.2.2 Stationary phase

- Nature : silicone oil DC 200 [of viscosity approximately 35×10^{-5} m^2/s (350 cSt)]
- Degree of impregnation : 40 g per 100 g of support [28 % (m/m)]
- Solvent : chloroform

Disperse the support in a solution of silicone oil in the chloroform. Then evaporate the solvent in an evaporator, purging under inert gas.

---

[1] ISO 6569, *Natural gas — Rapid analysis by gas chromatography*.

[2] Hydrocarbons up to heptane can be measured by increasing the temperature of the column from 70 to 150 °C at a rate of 2 °C/min.

[3] If the natural gas contains any hydrogen, helium, oxygen or carbon monoxide, these components cannot be determined by the method described and they interfere with the determination of nitrogen.

[4] In view of the dimensions of the tube, a form of two concentric helices is recommended. This allows the column to be mounted in any currently used chromatograph.

[5] The values specified for the stationary phase content, the particle size of the support and the flow rate of the carrier gas correspond to the optimum values observed during laboratory tests.

2.1.2.3 Particle size after impregnation : 250 to 300 µm

2.1.2.4 Conditioning

- Temperature : 180 °C
- Duration : 12 h
- Purging gas : nitrogen or helium at 60 ml/min

2.2 Injection device.

- Type : gas sampling valve
- Volume of the loop : 1 ml max.

2.3 Carrier gas.

- Nature : hydrogen or helium
- Purity : > 99,9 %
- Pressure reducing valve : two stage (second stage between 0 and 5 bar)

2.4 Detector.

- Type : thermal conductivity with filament

2.5 Recorder.

- Type : potentiometric or high imput impedance
- Sensitivity : 1 mV full scale
- Response time at full scale : approximately 1 s

2.6 Integrator.

This accessory is not strictly necessary but facilitates the acquisition and examination of chromatographic data.

Any electronic integrator capable of dealing with signals up to 1 V amplitude is suitable.

3 Procedure

3.1 Control of the apparatus

3.1.1 Column

Set the temperature to 70 ± 2 °C and the carrier gas flow rate to 60 ml/min, the effective inlet pressure being approximately 2 bar.

3.1.2 Detector

Set the temperature to 150 °C and set the current as specified in the manufacturer's instructions for the carrier gas used.

3.1.3 Recorder

3.1.3.1 Chart speed

If triangulation of the peaks is to be carried out, select the speed such that the width at half the height of the narrowest peak is at least 5 mm.

3.1.3.2 Adjustment of the zero

Disconnect the detector from the recorder, short-circuit the inlet terminals and adjust the recorder pen to 5 % of the full scale. Reconnect the detector to the recorder and, with the detector on and at the maximum sensitivity used, again bring the recorder pen to 5 % of the full scale.

If an integrator is not available, the attenuations should be selected such that each peak has a height which can be measured precisely.

3.2 Determination

After verification of the stability of the baseline at the maximum sensitivity used, introduce the test sample into the sample loop, at a rate of approximately 3 l/h and inject the sample (1 ml max.).

Check the performance of the column : a chromatogram similar to that shown in the figure shall be obtained; the height of the trough separating the nitrogen and methane peaks shall be less than or equal to 10 % of the height of the nitrogen peak.

3.3 Examination of the chromatogram

3.3.1 Qualitative analysis

The table gives the order of elution of the components and, for guidance, their retention times relative to *n*-butane.

Duration of analysis 25 min (up to *n*-pentane).

3.3.2 Quantitative analysis

3.3.2.1 Determine the areas of the peaks by one of the following methods :

a) manual examination : approximate the peaks to triangles, and calculate the areas from the formula :

height × width at half height × attenuation

Measure the width at half height to the nearest 0,1 mm.

b) by direct measurement using the integrator (2.6).

3.3.2.2 Calculate the concentrations of the components in the sample by the formula given in clause 4, correcting the peak areas by response coefficients. The method is applicable, since components not eluted from the chromatograph are, in this case, present in low concentrations.

It is convenient to use a table of coefficients; values are given in the table for the two carrier gases specified. For more accurate calibration, use a calibration gas mixture similar in composition to the natural gas to be analysed, and prepared by the weighing method (see ISO 6142)[1]. Calculate the response coefficients to be used. If one or several coefficients differ by more than 10 % from the values given in the table, the reason for this difference should be investigated.

4 Expression of results

Calculate the concentration, expressed as a molar percentage, of each component in the sample from the formula

$$C_i = \frac{A_i K_i}{\sum_{1}^{n} (A_i K_i)} \times 100$$

where

A_i is the area of the peak for component i;

K_i is the response coefficient for component i.

For this type of sample, the concentration as a molar percentage can be assumed to be the concentration as a percentage by volume, provided that the compressibility factor is not significantly different from 1.

5 Precision

5.1 Repeatability

If the integrator is used, the repeatability of the method, as a relative value, is

- for methane : of the order of 0,1 %;
- for other components in concentrations greater than 0,5 % molar : of the order of 0,5 to 1 %;
- for components in concentrations less than 0,5 % molar : of the order of 5 to 20 %.

5.2 Reproducibility

The reproducibility of the method, as a relative value, is 1 % for methane and of the order of 10 % for other components.

6 Test report

The test report shall include the following information :

a) a reference to this International Standard;

b) identification of the sample:

- origin,
- presumed composition,
- sampling conditions : date,
  pressure,
  temperature,
- cylinder number;

c) the results; composition of the sample by molar percentage;

d) any unusual features noted during the analysis;

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

Table

Component	K_i Carrier gas : hydrogen	K_i Carrier gas : helium	Retention time relative to *n*-butane
Nitrogen (N_2)	0,91	0,81	0,29
Methane (CH_4)	1	1	0,31
Carbon dioxide (CO_2)	0,80	0,75	0,35
Ethane (C_2H_6)	0,69	0,70	0,41
Propane (C_3H_8)	0,55	0,55	0,57
iso-Butane (i-C_4H_{10})	0,48	0,43	0,82
n-Butane (n-C_4H_{10})	0,47	0,42	1
neo-Pentane (neo-C_5H_{12})	0,47	0,42	1,10
iso-Pentane (i-C_5H_{12})	0,43	0,36	1,57
n-Pentane (n-C_5H_{12})	0,42	0,34	1,84

---

[1] ISO 6142, *Gas analysis — Preparation of calibration gas mixtures — Weighing methods.*

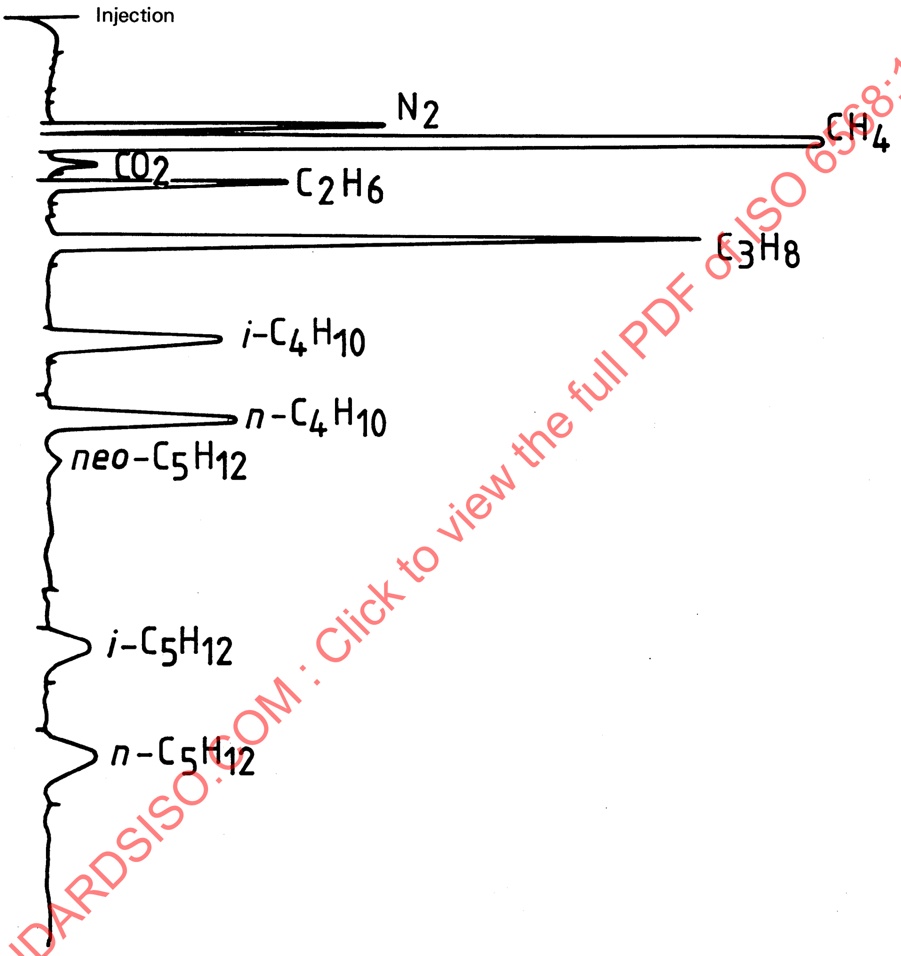

Figure — Typical chromatogram