International Standard ISO 6977

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Natural gas — Determination of water and methanol contents — Gas chromatographic method

Gaz naturel — Dosage de l'eau et du méthanol — Méthode par chromatographie en phase gazeuse

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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.

International Standard ISO 6977 was developed by Technical Committee ISO/TC 158, *Analysis of gases*, and was circulated to the member bodies in April 1982.

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

Australia
Belgium
Czechoslovakia
Egypt, Arab Rep. of
France
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Spain
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Netherlands

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Natural gas — Determination of water and methanol contents — Gas chromatographic method

0 Introduction

Water vapour may be present in natural gas for several reasons, for example as a result of storage in underground reservoirs or as a result of passing through mains containing moisture. The formation of hydrocarbon hydrates is prevented by injections of methanol.

1 Scope and field of application

This International Standard specifies a gas chromatographic method for the quantitative determination of water and methanol in natural gas.

The method is applicable for the determination of water and methanol contents in the range 20 mg to 1 g per cubic metre of gas under normal conditions. Determinations up to the point of saturation, at the temperature and pressure of the gas in the pipeline, are not, however, excluded. The method has been proved to be applicable to natural gas containing 10 g of hydrocarbons condensable at − 80 °C per cubic metre of gas.

2 Reference

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

3 Apparatus and materials

3.1 Gas chromatograph

Any apparatus with thermal conductivity detection is suitable, provided that the volume of the oven is sufficient to accommodate the column.

3.2 Injection device

The injection device shall consist of a six-way rotary valve and a loop of volume 5 ml, made of glass or glass-lined stainless steel. The following two types of valve are suitable.

3.2.1 Valves made entirely of polytetrafluoroethylene (PTFE), operating at room temperature (with a glass loop).

3.2.2 Valves made of stainless steel and polytetrafluoroethylene (PTFE), operating at the temperature of the column (with a heated stainless steel loop). In this case, control of the operating mechanism of the valve shall be placed outside the oven.

3.3 Chromatographic column

3.3.1 Tube

- Material: copper, stainless steel, polytetrafluoroethylene (PTFE)[1]
- Length: 2,5 m
- Diameter: 4 to 5 mm internal diameter
  6 to 7 mm external diameter

3.3.2 Packing

3.3.2.1 Support

- Nature: Chromosorb T
- Particle size: 250 to 500 µm (60 to 30 mesh)

3.3.2.2 Stationary phase

- Nature: Carbowax 4000

3.3.2.3 Preparation of the column

— Degree of impregnation: 10 g per 100 g of support. Dissolve the stationary phase in chloroform before impregnation.

— Filling: Take care to cool the impregnated support before filling the column, according to the appropriate packing technique.

— Conditioning: 24 h at 150 °C with dry carrier gas purging the column.

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[1] If the gas contains more than 1 % of acidic sulphur compounds, glass or PTFE should preferably be used.

3.4 Carrier gas

Helium containing less than 50 ppm by volume of impurities, dried by passing through a trap filled with molecular sieve 5A at ambient temperature. The reducing valve shall be fitted with a stainless steel diaphragm.

3.5 Potentiometric recorder

- Sensitivity: 1 mV full scale
- Response time: 1 s

3.6 Integrator

- Input signal: appropriate to the chromatograph
- Integration: tangential

3.7 Automatic apparatus

The whole apparatus can be entirely automated. In this case, injection of the gas sample by the sampling valve is sequential and the only manual intervention consists in changing the gas injected (gas sample, calibration gas mixture).

Injections are started by means of a control box which converts electrical signals to pneumatic signals. They are started by the programming of the integrator. The frequency of injection is one injection every 15 min.

NOTE — An example of a chromatogram obtained using automatic apparatus for the determination of water and methanol in natural gas is shown in the figure.

4 Sampling

Water is widely distributed in the environment, either as vapour or adsorbed on to, or absorbed into, various materials. For this reason great care shall be taken in the design and manufacture of the apparatus and, especially, of the transfer lines, in order to avoid introducing a systematic error into the result.

The specified performance is guaranteed only for those samples taken on line with the analytical chain placed close to the line containing the natural gas to be analysed.

5 Procedure

5.1 Setting up the apparatus

5.1.1 Column

a) Carrier gas

- Flow rate: 40 ml/min
- Inlet pressure: 30 kPa*

b) Temperature: 110 ± 2 °C

5.1.2 Detector

- Temperature: 150 °C
- Filament current: adjusted to the maximum sensitivity allowed by the manufacturer.

5.2 Calibration

5.2.1 Calibration gas mixtures

The following two mixtures may be used.

5.2.1.1 Reference mixture

This is a calibration gas mixture prepared dynamically at the place of use using a permeation bench (see ISO 6349) with water and methanol permeation tubes installed in its oven.

The complementary gas of the calibration gas mixture should preferably be pure dried methane or nitrogen. The concentration of the components of the reference gas mixture should be of the same magnitude as that of the gas to be analysed.

5.2.1.2 Secondary reference mixture

This is a calibration gas mixture under compression in a cylinder. The concentrations of the components of the mixture are derived by comparison with the mixture from the permeation bench. It can be used as a secondary reference mixture provided that:

- the concentration of each component does not change during storage;
- sampling is carried out with care; the flow rate shall be adjustable only by means of a high pressure needle valve.

5.2.2 Chromatography of reference mixture

Inject the reference mixture several times until the values remain constant within the repeatability of the method.

Since the operating conditions are fixed, this operation is intended for measuring the retention times and peak areas (t_{Ri} and A_i) for water and methanol.

5.2.3 Chromatography of sample

Inject the same volume of sample as reference mixture. Measure the retention times and peak areas (t_{RE} and A_E).

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* 30 kPa = 0,3 bar