INTERNATIONAL STANDARD

ISO 10101-3

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Natural gas — Determination of water by the Karl Fischer method —

Part 3: Coulometric procedure

Gaz naturel — Dosage de l'eau par la méthode de Karl Fischer — Partie 3: Méthode coulométrique

Reference number
ISO 10101-3:1993(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established 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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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.

International Standard ISO 10101-3 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Sub-Committee SC 1, *Analysis of natural gas*.

ISO 10101 consists of the following parts, under the general title *Natural gas — Determination of water by the Karl Fischer method*:

— *Part 1: Introduction*

— *Part 2: Titration procedure*

— *Part 3: Coulometric procedure*

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Natural gas — Determination of water by the Karl Fischer method —

Part 3:
Coulometric procedure

WARNING — Local safety regulations must be taken into account, when the equipment is located in hazardous areas. Due to the toxicity and odour of pyridine, the user should ensure that there is adequate ventilation.

1 Scope

This part of ISO 10101 specifies a coulometric procedure for the direct determination of water content by the Karl Fischer method. The method applies to natural gas and other gases which do not react with Karl Fischer reagents.

It applies to water concentrations between 5 mg/m^3 and 5 000 mg/m^3. Volumes are expressed a temperature of 273,15 K (0 °C) and a pressure of 101,325 kPa (1 atm).

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 10101. 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 10101 are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

ISO 10101-1:1993, *Natural gas — Determination of water by the Karl Fischer method — Part 1: Introduction.*

3 Principle

A measured volume of gas is passed through the titration cell, where the water is absorbed by the anodic solution. The iodine required for the determination of water by the Karl Fischer reaction is generated coulometrically from iodide. The quantity of electricity is directly proportional to the mass of iodine generated and hence to the mass of water determined.

The principle and chemical reactions of the Karl Fischer method are given in ISO 10101-1:1993, clauses 3 and 4; interferences are also described in clause 4 of ISO 10101-1.

4 Reagents

4.1 Reagents specially formulated for coulometric determination.

NOTE 1 A typical composition of the anodic solution is as follows: 34 % (*m/m*) trichloromethane, 3 % (*m/m*) tetrachloromethane, 22 % (*m/m*) methanol, the remainder being sulfur dioxide and pyridine.

Other reagents may be used, for the coulometric determination by the Karl Fischer method, if they have shown to be satisfactory.

4.2 Reference solution, e.g. water and methanol mixture, with a water content of 5,0 mg/l ± 4 % or 10,0 mg/l ± 4 %. Keep this solution in a flask sealed with a septum.

4.3 Phosphorus pentoxide, with indicator.

5 Apparatus

A diagram of the titration cell is shown in figure 1 and a diagram of the complete apparatus is shown in figure 2. Figures 3 and 4 illustrate the gas inlet with 3-way valve and the drying tube in the gas outlet line, respectively.

All parts which come into contact with gas shall consist of glass and stainless steel. Flexible connections shall be polychloroprene or fluoroelastomers. The rotor of the gas inlet tap shall be of polytetrafluoroethylene.

6 Sampling

See ISO 10101-1:1993, clause 5.

7 Procedure

7.1 Installation

Follow the manufacturers' instructions for the addition of reagents to the cells, for switching on and for the determination of any initial water.

7.2 Testing the response

Flush a 10 µl syringe twice with reference solution (4.2) and introduce a measured amount (about 10 µl) into the anodic cell with the tip of the needle below the surface of the liquid. Switch on the stirrer and start the determination.

The results, expressed in micrograms, should agree with the mass of water introduced with the reference solution to within the expected repeatability. If sufficiently good agreement does not exist, look for a technical defect in the apparatus and resolve it before use.

7.3 Measurement

Switch on the magnetic stirrer. Purge the sample line to atmosphere through the 3-way valve. Adjust the 3-way valve to direct gases into the titration vessel and adjust the gas flow to between 30 l/h and 40 l/h. Measure the flow at the exit from the cell with a wet gas meter. The gas volume to be used depends upon the anticipated concentration of water. When this volume has passed through the cell, return the 3-way valve to the former position.

NOTE 2 The optimum flowrate depends on the geometry of the equipment. A check that all the water is being absorbed should be carried out by passing the same volume of gas at different flowrates and ensuring that equal results are obtained.

For low water concentrations, it may be preferable to delay the determination until the required volume has been passed. The delayed determination procedure can only be applied if it is available as a programmable feature on the coulometer, which then continues to compensate for the background over the time entered into the memory. if this procedure is used, the operator should be satisfied that automatic compensation for zero drift is still correctly applied. The drift should be constant during the whole time of the determination.

7.4 Blank determination

In the case of water concentrations (less than 100 mg/m^3), perform a blank determination to correct for losses of iodine by evaporation during passage of the gas sample. To this end, install an absorber packed with phosphorus pentaxide (4.3) as close as possible to the inlet of the titration cell. Pass through an amount of dry gas, under the same conditions as those applied for the actual sample (flow, time, pressure and temperature). Repeat blank determinations until a constant level is achieved.

NOTE 3 The water vapour concentration at equilibrium with phosphorus pentoxide amounts to 0,2 mg/m^3. Under ambient conditions, iodine losses by evaporation will be equivalent to water concentrations of 1 mg/m^3 to 4 mg/m^3.

The contents of the absorber should be replaced when the coloured zone occupies more than 50 % of the absorber length.

8 Expression of results

8.1 Method of calculation

Calculate the water content $\varrho(H_2O)$, expressed in milligrams per cubic meter at 273,15 K (0 °C) and 101,325 kPa (1 atm), of the gas using the equation

$$\varrho(H_2O) = \frac{(m_1 - m_0)(273{,}15 + \theta_A) \times 101{,}325}{V_A(p_A - p_W) \times 273{,}15}$$

where

m_0 is the mass, in micrograms, of water obtained during the blank determination;

m_1 is the mass, en micrograms, of water obtained during the sample determination;

θ_A is the temperature, in degrees Celsius, of the gas in the wet-test gas meter;

V_A is the volume, in litres, of gas passed through the cell;

p_A is the absolute pressure, in kilopascals, of the gas in the wet-test gas meter;

p_W is the vapour pressure, in kilopascals, of water at temperature θ_A.

If necessary, the water content can be corrected for interferences due to sulfur coumpounds as described in ISO 10101-1:1993, clause 4. Express the water content as $\varrho(H_2O)$, in milligrams per cubic metre, choosing the number of significant figures according to the value of the repeatability.

8.2 Precision

8.2.1 Repeatability, r

If one operator determines two different results under repeatable conditions, both results shall be considered as acceptable and in accordance with this part of ISO 10101, provided that they do not differ by more than the numerical value of r shown graphically in figure 5, determined according to ISO 5725.

8.2.2 Reproducibility, R

If different laboratories determine results under comparable conditions, both results shall be considered as acceptable and in accordance with this part of ISO 10101, provided that they do not differ by more than the numerical value of R shown graphically in figure 5, determined according to ISO 5725.

9 Test report

The test report shall contain at least the following information:

a) a reference to this part of ISO 10101;

b) the date and time of sampling or measurement;

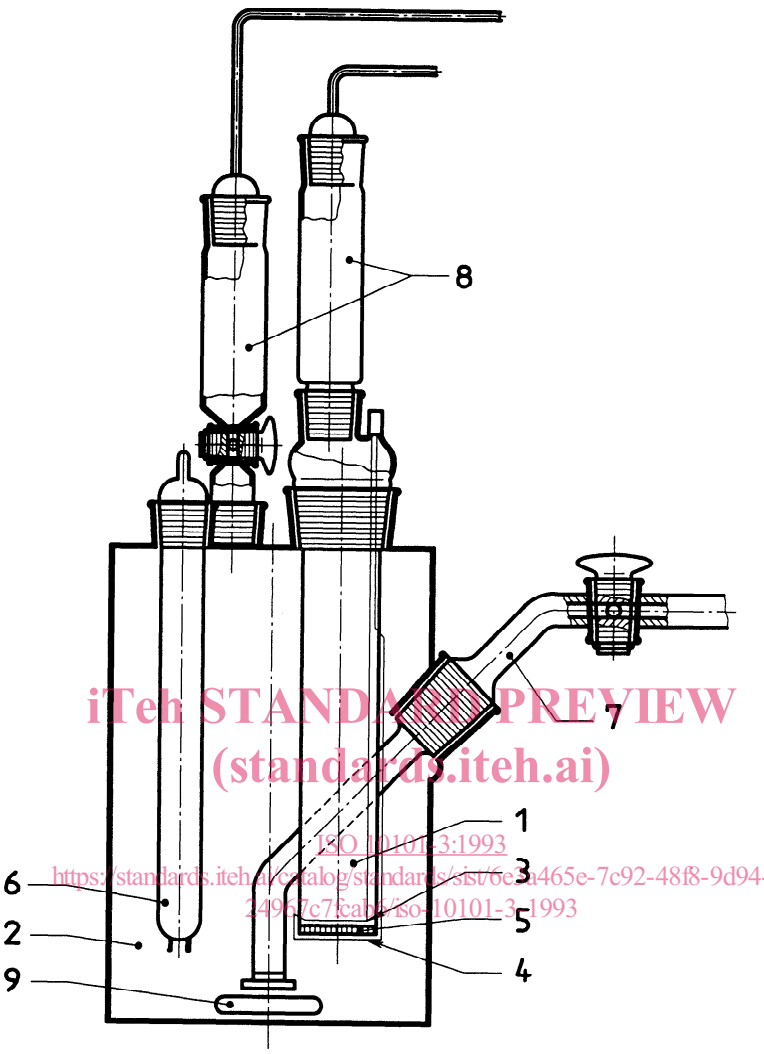
c) the place of sampling or measurement;

d) whether the analysis was performed on-site, or on a sample returned to the laboratory;

e) the temperature and pressure of the gas stream at the time of sampling or analysis;

f) the concentration of, and correction for, any interfering substances in the gas;

g) any deviation from the procedure specified.



1 Cathodic cell
2 Anodic cell
3 Cathode
4 Anode
5 Diaphragm
6 Platinium double electrode
7 Gas inlet
8 Drying tubes
9 Magnetic stirrer

Figure 1 — Titration cell

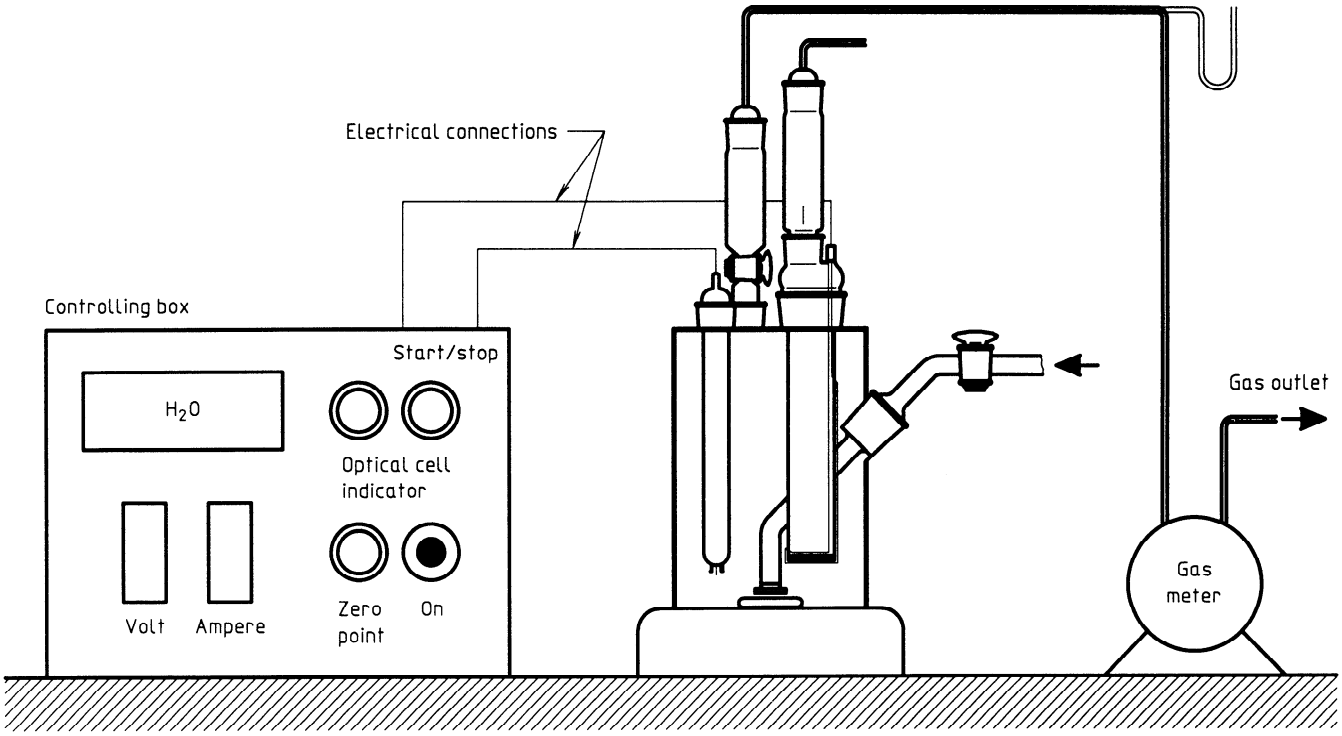


Figure 2 — Karl Fischer apparatus for coulometric determination — Typical assembly

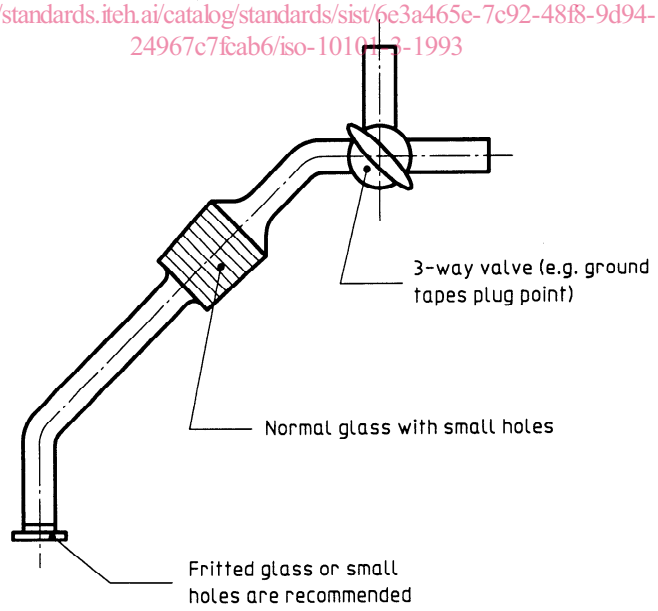


Figure 3 — Gas inlet with 3-way valve

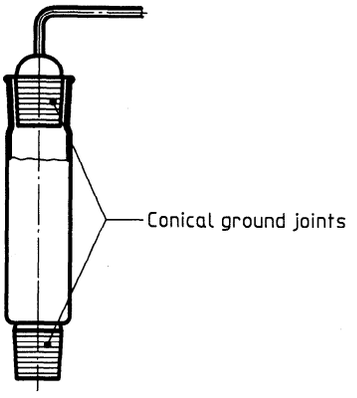


Figure 4 — Drying tube in the gas outlet line

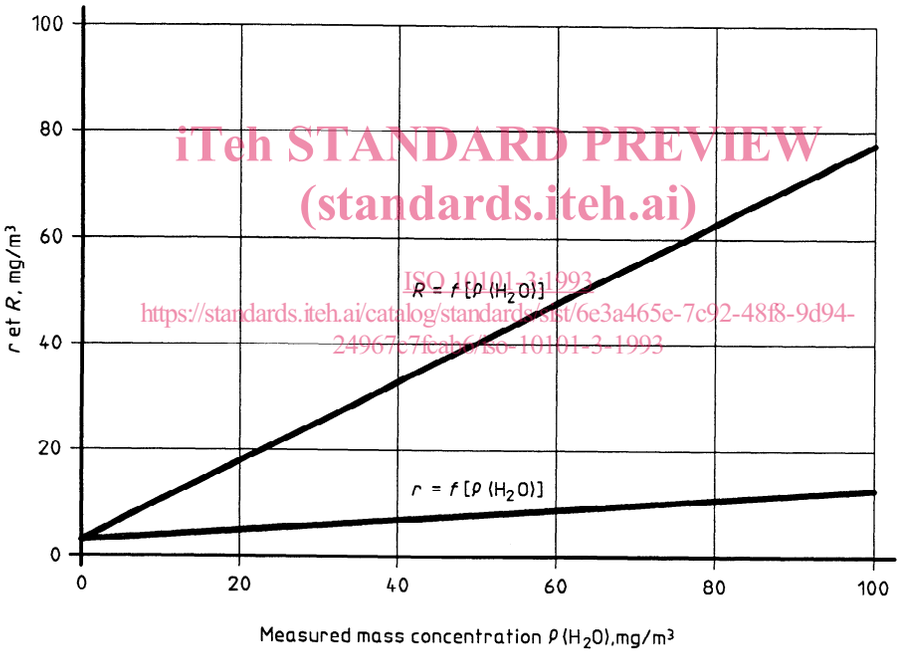


Figure 5 — Repeatability r and reproducibility R

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