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

Part 2:
Volumetric procedure

Gaz naturel — Dosage de l'eau par la méthode de Karl Fischer —
Partie 2: Méthode volumétrique

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 193, *Natural Gas*, Subcommittee SC 1, *Analysis of natural gas*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 238, *Test gases, test pressures, appliance categories and gas appliance types*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 10101-2:1993), which has been technically revised.

The main changes are as follows:

- Clause 2 and Bibliography were revised;
- New fixed structure numbering inserted;
- Clause 5 was modified;
- Clause 9 was modified;
- 10.2 was modified.

A list of all parts in the ISO 10101 series can be found on the ISO website.

Introduction

Water vapour may be present in natural gas due to, for example, natural occurrence in the well production stream, the storage of gas in underground reservoirs, transmission or distribution through mains containing moisture or other reasons.

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

Part 2:
Volumetric procedure

WARNING — Local safety regulations should be taken into account, when the equipment is located in hazardous areas.

1 Scope

This document specifies a volumetric procedure for the determination of water content in natural gas. Volumes are expressed in cubic metres at a temperature of 273,15 K (0 °C) and a pressure of 101,325 kPa (1 atm). It applies to water concentrations between 5 mg/m^3 and 5 000 mg/m^3.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 383, *Laboratory glassware — Interchangeable conical ground joints*

ISO 10101-1, *Natural gas- Determination of water by the Karl Fischer method – Part 1- Introduction*

ISO 14532, *Natural gas — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 14532 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at https://www.electropedia.org/

4 Principle

A measured volume of gas is passed through a cell containing a relatively small volume of absorbent solution. Water in the gas is extracted by the absorbent solution and subsequently titrated with Karl Fischer reagent. The design of the cell and the absorbent solution are chosen to ensure efficient collection of the water at the high flowrates necessary.

The principle and chemical reactions of the Karl Fischer method are given in ISO 10101-1:2020, Clauses 4 and 5; interferences are also described in ISO 10101-1:2020, Clause 5.

ISO 10101-1:2020, Clause 5 describes interfering substances which may be present in natural gas and corrections for the interference of hydrogen sulfide and mercaptans.

5 Reagents

5.1 Karl Fischer reagent, of which the water equivalent is approximately 5 mg/ml.

NOTE For most applications, commercially available Karl Fischer (KF) reagent with a water equivalent of approximately 5 mg/ml has been found adequate.

The reagent can be bought as a one-component reagent, which contains all the necessary reagents (iodine, sulfur dioxide and the base (e.g. imidazole)) dissolved in an anhydrous solvent (methanol or 2-methoxyethanol) or it can be provided as two-component reagent, i.e. a solvent reagent and a titrant reagent which are mixed before use.

The solvent reagent contains sulfur dioxide and a base (e.g. an alkali or alkaline earth metal benzoate, ammonia, imidazole). The titrant reagent contains iodine. The two-component reagent provides a stable titre as long as any moisture is prevented from entering into the reagents and a better shelf life.

If required, it may be prepared following the procedure in 5.1.1.

5.1.1 Preparation of Karl Fischer reagent

5.1.1.1 Components

5.1.1.1.1 Methanol, with a water content of less than 0,01 % (mass fraction). Use commercially available dry methanol, anhydrificated in the lab by one of the following procedures

5.1.1.1.1.1 Place 2 l of methanol in a two-neck 3 l flask and add 10 g of magnesium turnings. Add a crystal of iodine, connect the flask to a reflux condenser and leave overnight. Next day, add a further 5 g of magnesium turnings and reflux for 1 h. Connect the top of the reflux condenser to a still head, a double surface condenser and a collection flask. Disconnect the water flow through the condenser originally used for reflux and distil the contents of the flask. Discard the first 150 ml of condensate. Distil the rest into dried 1 litre flasks. Vent the system through a drying tube during distillation.

5.1.1.1.1.2 Dry the methanol over a freshly activated molecular sieve.

5.1.1.1.2 2-Methoxyethanol, with a water content of less than 0,01 % (mass fraction).

NOTE This can be used as an alternative to methanol (5.1.1.1.1) with a lower vapour pressure and therefore less losses due to evaporation during sampling of the gas

5.1.1.1.3 Imidazol, anhydrous.

5.1.1.1.4 Sulfur dioxide, liquefied and dry.

5.1.1.1.5 Iodine.

5.1.1.4 Preparation

Measure 300 ml of dry methanol (5.1.1.1.1) or 2-methoxyethanol (5.1.1.1.2) and 110 ml of anhydrous imidazole (5.1.1.1.3) into a 750 ml conical flask. Slowly pass liquid sulfur dioxide (5.1.1.1.4) into this solution, mixing carefully until the increase in weight is 43 g. Cool this solution in a freezing mixture. When cool, add sufficient iodine (5.1.1.1.5) to give a permanent light brown colour. Then add 63 g of iodine and swirl until dissolved. Make up to 500 ml with dry methanol or 2-methoxyethanol. Leave standing in the stoppered conical flask for 24 h before use. Commercial reagents, when aged, may give a slow response near the end point.

5.2 Absorbent solution.

5.2.1 Components

5.2.1.1 Ethylene glycol, with a water content less than 0,1 % (mass fraction).

5.2.1.2 Sulfur dioxide, liquefied and dry.

5.2.1.3 Imidazol, anhydrous

5.2.1.4 Karl Fischer reagent (see 5.1).

5.2.2 Preparation of the absorbent solution

Slowly add 20 g of sulfur dioxide (5.2.1.2) to 180 ml of anhydrous imidazole (5.2.1.3), while mixing carefully (solution A).

To prepare the absorbent solution, add 55 ml of dry ethylene glycol (5.2.1.1), 55 ml of Karl Fischer reagent (5.2.1.4) and 73 ml of solution A to a round bottomed flask. Boil under reflux for 10 min with a drying tube on the condenser, and then cool.

5.3 Reference solution, e.g. water and methanol mixture, with a water content of 5,0 mg/l ± 0,2 mg or 10,0 mg/l ± 0,4 g. Keep this solution in a flask sealed with a septum.

NOTE There are reference solutions commercially available. They consist of stable solvent mixtures with specific composition and precisely determined water content, supplied in airtight glass ampoules to ensure quality when opened by the end user. The exact amount of water is given on the certificate of analysis. Typically, the reference solutions are filled under Argon in 4 ml or 8 ml glass ampoules.

6 Apparatus

6.1 Karl Fischer apparatus, as described in Annex A.

6.2 Wet-test gas meter, accurate to ±1 % of the volume passed.

6.3 Guard tube, or Durand bottle, packed with anhydrous calcium chloride (or another suitable drying agent).

NOTE This is used to prevent back diffusion of water vapour from the gas meter to the titration cell.

6.4 Titration cell, as shown in Figure A.1.

6.5 Glass syringe, of 20 ml.

NOTE Absorbent solution is most easily added to and removed from the cell by means of a 20 ml graduated syringe with a 6 % (Luer) fitting and hypodermic needles of suitable length and 1 mm to 2 mm bare.

6.6 Syringe, with a fixed needle, of 10 µl, for standardization of the Karl Fischer reagent.

7 Determination of the water equivalent of the Karl Fischer reagent

7.1 Determine the water equivalent of the Karl Fischer reagent daily or before use, as appropriate, in line with 7.2 to 7.5.

7.2 Using a dry syringe, introduce sufficient absorbent solution (5.2) to cover the electrodes in the apparatus (5.1). Switch on the apparatus and start the stirrer motor. Add the Karl Fischer reagent (5.1) until the needle settles down at a position near zero. When this point is reached, cease additions, since additions of large amounts of reagent will only move the electrometer about 0,02 V. To achieve maximum sensitivity at this first stable point, adjust the zero control until the electrometer needle is at zero. Shake the cell several times so that all the internal surfaces are wetted. Once again, adjust to the zero position by adding more reagent. Repeat the procedure until the needle remains steady at the zero position for at least 30 s.

NOTE The meter needle will remain at zero for at least 30 s when the titration end point is reached.

7.3 Using the 10 µl syringe (6.6), add exactly 10 µl of reference solution (5.3) to the contents of the cell (6.4) (with the syringe needle below the surface of the absorbent solution) titrate to the zero position and note the volume of reagent used. Once again, shake the cell several times and if the electrometer needle shifts, titrate back to zero. Ignore this additional volume of Karl Fischer reagent; it represents any water which may have entered the cell as vapour while the 10 µl of reference solution was being added

7.4 Add a further 10 µl of water to the cell, and again titrate to the zero position. Take an average of the two titrations. If the variation is greater than 2 %, discard the contents of the cell. Introduce a further portion of absorbent solution into the cell and repeat the standardization procedure. If the titration for two further 10 µl portions of distilled water still varies by more than 2 %, it is likely that the Karl Fischer reagent has aged and needs replacing with fresh reagent.

Check the delivery of the 10 µl syringe by weighing it, using a balance capable of weighing to ±0,1 mg. Ensure that the weighings are within 1 %.

7.5 Calculate the water equivalent T, expressed in milligrams of water per millilitre, of the Karl Fischer reagent using the following Formula (1):

$$T = m / V \tag{1}$$

where

m is the mass, in milligrams, of water added;

V is the volume, in millilitres, of Karl Fischer reagent required for the titration of the added water.

A commercially available water standard may be used instead of distilled water.

8 Sampling

Use the procedure described in accordance with ISO 10101-1.

9 Procedure

9.1 The apparatus may be used in the laboratory, or outside on the processing plant, with appropriate precautions.

NOTE The differences between these approaches are described in 9.4. Because of the difficulty of sampling gas streams without altering their water content, the equipment is likely to be used more frequently outside the laboratory.

Whether the determination is executed inside or outside the laboratory, the first determination is likely to be erroneous, due to the uncertainties associated with connecting the sample stream and purging the sampling lines. For this reason, repeat determinations are necessary on a sample stream flowing continuously at 1 l/min.

9.2 Remove the contents of the cell (6.4) and add 20 ml of the absorbent solution (5.2) to the titration cell using a dry syringe (6.5). If necessary, add enough water until the meter shows an excess of water and titrate back to zero with Karl Fischer reagent (5.1).

9.3 Close the gas inlet socket with a 7/16 ground glass stopper, and the gas outlet with a 5/13 ground glass stopper. Shake the cell several times so that all the internal surfaces are "wetted" and again adjust to the zero position by adding more reagent. Repeat this procedure until the needle remains steady at the zero position.

9.4.1 and 9.4.2 refer to the use of the equipment in the laboratory, or on the plant, respectively.

9.4.1 Switch off the stirrer and proceed to 9.5. If the sample is being taken from a line which is continuously purged, the time of purging indicated in 9.4 can be reduced.

9.4.2 In the laboratory, disconnect the apparatus from the mains supply, switch to battery operation and check that the batteries are satisfactory. Turn off the stirrer and ensure that the switch is set to "READ". The apparatus is now ready to take onto the plant.

WARNING — The equipment is neither flameproof nor intrinsically safe. Local safety regulations shall be taken into account when using the equipment in hazardous zones. As a minimum precaution, a test for flammable gases should be made in the area in which it is to be used.

9.5 Open the sampling point valve and purge the line for 5 min at about 10 l/min. Connect the wet-test gas meter (6.2) to the same point and adjust the flow to the required flow rate (1 l/min for streams containing less than 50 mgH_2O/m^3). Allow to purge for a further 30 min.

9.6 Disconnect the wet-test gas meter and connect the gas inlet tube of the cell to the sample point, using a metal coupling (with polychloroprene "O" rings) that is capable of connecting glass to glass or metal to glass.

Alternatively, the gas flow rate may be metered before the determination and the gas volume can be calculated by the time of the sample introduction.

Under no circumstances shall lengths of PVC or similar types of tubing be used to connect the sample point to the cell. This type of tubing will allow diffusion of water into the sample.

It is recommended to introduce the gas directly into the titration cell through a capillary that is submerged as deep as possible into the cell.

9.7 Connect the outlet of the calcium chloride guard tube (6.3) to the wet-test gas meter and the inlet to the cell outlet.

Flexible tubing may be used for the connection.

9.8 Connect the cell to the gas stream by inserting the gas inlet tube through the 7/16 conical joint as in ISO 383 and allow the gas to pass through the cell for 5 min, adding reagent as necessary to maintain the cell contents at the meter zero position.

9.9 Record the wet-test gas meter reading at a convenient moment when the voltmeter reading is on zero. Record the burette reading (to the nearest 0,002 ml) associated with this volume of gas. This first titration can be ignored, as the result is very likely to be erroneous.

9.10 Without interruption to the flow, pass an additional volume of sample (10 litres in the case of gases containing H_2O mass concentration of less than 50 mg /m^3) through the cell, once again adding reagent to maintain the voltmeter at or near the zero position throughout the titration. Record the wet-test gas meter reading at a moment when the voltmeter is on zero, and the corresponding burette reading (to the nearest 0,002 ml). Record the temperature and pressure of the gas in the wet-test gas meter.

9.11 Repeat the procedure described in 9.10 as many times as is necessary to obtain a constant reading (a minimum of four titrations).

10 Expression of results

10.1 Method of calculation

Calculate the water content $\rho(H_2O)$, expressed in milligrams per cubic meter at 273,15 K (0 °C) and 101,325 kPa (1 atm), of the gas using Formula (2):

$$\rho(\mathrm{H_2O}) = \frac{1\,000 \times V \times T\,(273{,}15 + \theta_\mathrm{A}) \times 101{,}325}{V_\mathrm{A}\,(p_\mathrm{A} - p_\mathrm{W}) \times 273{,}15} \quad (2)$$

where

V is the volume, in millilitres, of reagent required;

T is the water equivalent, in milligrams of water per millilitre, of the KF reagent calculated in 7.5;

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

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

If necessary, the observed water content can be corrected for interferences due to sulfur compounds as described in ISO 10101-1:2022, Clause 5.

10.2 Measurement uncertainty

For this method, an interlaboratory comparison (method validation study) according to ISO 5725-2 has not yet been carried out. Therefore a “collaborative” estimate of the uncertainty of measurement results according to ISO 10101-1:2022, Clause 7 is not available.

Thus, the user has to provide an individual estimate of the uncertainty of his measurement results, e.g. using the GUM approach, based on a comprehensive uncertainty budget (see ISO/IEC Guide 98-3). Preferably, the estimate should include the contribution of sampling uncertainty. If this is not the case, this shall be clearly stated.

NOTE The standard deviation from replicate measurements is not a suitable uncertainty estimate, since it excludes major uncertainty contributions.

11 Test report

The test report shall contain at least the following information:

a) a reference to this document, i.e. ISO 10101-2:2022;

b) the date and time of sampling of measurement;

c) the place of sampling of measurement;

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

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

f) the concentration of, and correction for, any interfering substances in the gas when available or they are known;

g) any deviation from the procedure specified.

Annex A
(informative)

Karl Fischer apparatus

A.1 Burette

The burette is a piston-type of capacity 5 ml with a two-way PTFE key, which is attached to the base of the apparatus. The burette scale is subdivided every 0,005 ml. It is possible to estimate the burette reading to the nearest 0,002 ml. A suitable automatic burette, the performance of which is at least as good as this, may be used.

A.2 Reservoir

This is a modified 250 ml Durand bottle protected by a drying tube as shown in Figure A.2. The connection between the reservoir and the burette is a butt-joint, sealed with neoprene tubing.

A.3 Titration cell

This cell is fitted with two 7/16 ground glass conical joints as in ISO 383 for the gas inlet tube and the reagent delivery tube, a 5/13 ground glass conical joint for the gas outlet and a screwed connector for the electrode. If required, a further connection can be made, at an angle on the side of the cell, for a septum.

The ground glass connectors are not lubricated (the seal is made by the reagent as the cell is shaken to wet the internal surfaces). The gas inlet tube has an internal diameter of 2,5 mm and extends to within 5 mm of the cell base. The flexible lead from the burette is drawn to a fine jet, of 0,2 mm internal diameter, to prevent diffusion of the reagent into the cell.

NOTE A flexible polyethylene burette lead is necessary so that the cell can be shaken without disturbing any connections. During the normal duration of use, diffusion of moisture through the tubing is negligible. If the reagent is left in the tubing for some time, it is flushed out thoroughly before use.

A.4 Base

The base of the apparatus contains the electronic circuits of which a diagram is shown in Figure A.3 and a magnetic stirrer.

NOTE 1 The electronics function as follows:

When an excess of water is present, the electrodes are polarized and the impedance across them becomes of the same order as the 1 MΩ resistor. The voltmeter thus indicates about 0,5 V. When an excess of Karl Fischer reagent is present, the electrodes are depolarized and the impedance across them becomes very small compared with the 1 MΩ resistor. The voltmeter will now indicate 0 V. This circuit gives a very much sharper end-point indication than the more usual current measuring circuits.

NOTE 2 Experience has shown that it is necessary to use a magnetic stirring bar of 20 mm to 25 mm length, to ensure adequate mixing of the cell contents.