INTERNATIONAL STANDARD

**ISO 10101-3**

Second edition
2022-08

# 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*



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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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# Contents

Page

# Foreword

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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).

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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 10101-3:1993), which has been technically revised.

The main changes are as follows:

— Clause 2 and Bibliography were revised;

— new fixed structure numbering inserted;

— Subclause 9.2 Measurement of uncertainty was added.

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.

The Karl Fischer (KF) titration can be divided into two basic techniques – depending on the application range – volumetric and coulometric KF titration. The two analysis techniques differ in the mode of iodine addition or generation. Volumetric KF titration is preferably used for the determination of large amounts of water in the range of 1 mg to 100 mg. Coulometry, however, is a micro-method which is particularly well suited for determination of quantities of water from 10 µg to 10 mg.

Modern KF coulometers cover a range from 10 µg to 200 mg of water. Usually a resolution of 0,1 µg of water is achieved.

In coulometric water determination, iodine is not added in the form of a titrating solution but rather directly produced from an iodine-containing solution by an anodic oxidation reaction. The high analytic precision at low absolute water quantities makes coulometric KF titration particularly well suited for determination of the water content in aqueous gases.

Coulometric KF titration can be subdivided according to two distinct designs of the analysis cell: Cells with and without diaphragm. In both variants, the measuring cells are made of a titration vessel tightly sealed to prevent moisture ingress. The sample gas is passed directly through a glass frit into the KF titration cell. Thus, absorption of moisture from the environment is prevented and the gas finely dispersed. The fine distribution of the gas in the hygroscopic KF solution provides a large surface for material exchange, so that the water contained in the gas can be fully absorbed by the solution and then titrated. In the version with a diaphragm, the cell is divided into a large anode and a small cathode compartment, each filled with different reagents. Spatial separation is achieved by means of the diaphragm. In both compartments platinum electrodes are installed, via which a working current is passed through the titration cell. Due to the applied current, at the anode iodine is formed, which immediately reacts with the absorbed water from the gas sample. When all the water has been consumed by the reaction, an excess of iodine is formed that will be detected voltametrically, ending the titration. The amount of electricity consumed can be used to directly calculate, using Faraday's law, the quantity of water.

$$m_{H_2O} = \frac{M_{H_2O} \cdot Q}{z \cdot F}$$

where

$z$ is the number of exchanged electrons;

$M_{H_2O}$ the molecular weight of water;

$F$ the Faraday constant (96 485 C/mol);

$Q$ the charge which has flowed in C.

In the KF titration cell variant without a diaphragm there is no separation between the anode and cathode chambers. Thus, for the filling of the cell only one reagent is needed and used. In order to prevent direct reduction of iodine at the cathode, the cathode and anode are spatially separated from each other by a large distance. The use of the cell without a diaphragm has the advantage that the titration cell is easier to clean and only one reagent is consumed, whose replacement can be completely automated. In addition, unlike in cells with a diaphragm, during longer downtimes no moisture can accumulate in the diaphragm, making the titration cell faster to become operational. For the measurement of extremely low water contents (few ppm of water), the leading KF equipment manufacturers recommend, despite these advantages, use of a KF coulometer with diaphragm. For practical implementation, however, this adds possible sources of error, complication and prolongation of the measurement times.

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

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

# Part 3: Coulometric procedure



## 1 Scope

This document specifies a coulometric procedure for the determination of water content by the Karl Fischer method. The method is applicable to natural gas and other gases which do not react with Karl Fischer (KF) reagents.

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

## 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 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 the titration cell, where the water is absorbed by the anodic solution. The iodine required for the reaction with the water in the sample is generated in situ (in the titration beaker) using a reagent solution containing 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.

## 5 Reagents

### 5.1 Reagents specially formulated for coulometric determination.

The reagent does not need to be standardised, as coulometry is an absolute method. For a coulometric determination in the case of a cell with a diaphragm, two reagent solutions, an anolyte and a catholyte,

are required. The anolyte is inserted into the anode space of the cell and the catholyte into the cathode space.

### 5.2 Reference solution.

The recommended reference solution, e.g. water and methanol mixture, has a water content and uncertainty of 10 mg/g and 1 %, respectively. Alternative with a water content of 5,0 mg/l ± 4 % or 10,0 mg/l ± 4 % may be applied.

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.

### 5.3 Commercially available dry cartridges.

For example, filled with phosphorus pentoxide.

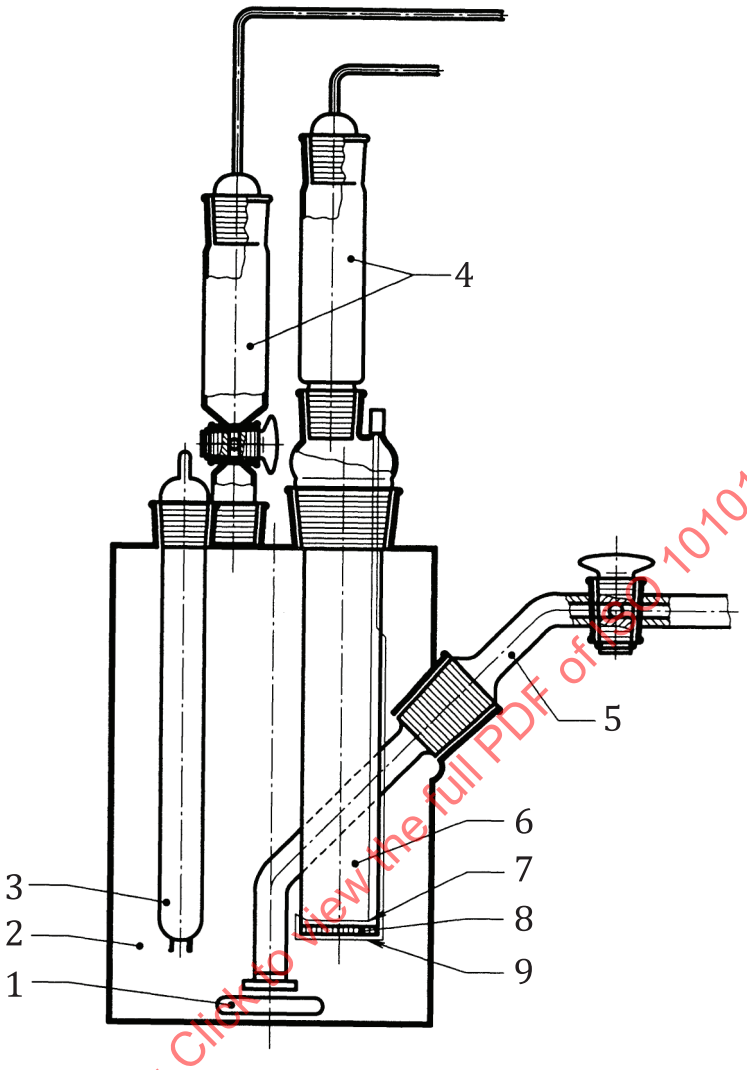
## 6 Apparatus

### 6.1 Diagram of the complete apparatus is shown in Figure 1.

**6.1.1 Titration cell,** as shown in Figure 1.

**6.1.2 Gas inlet**, with a 3-way valve as in Figure 3.

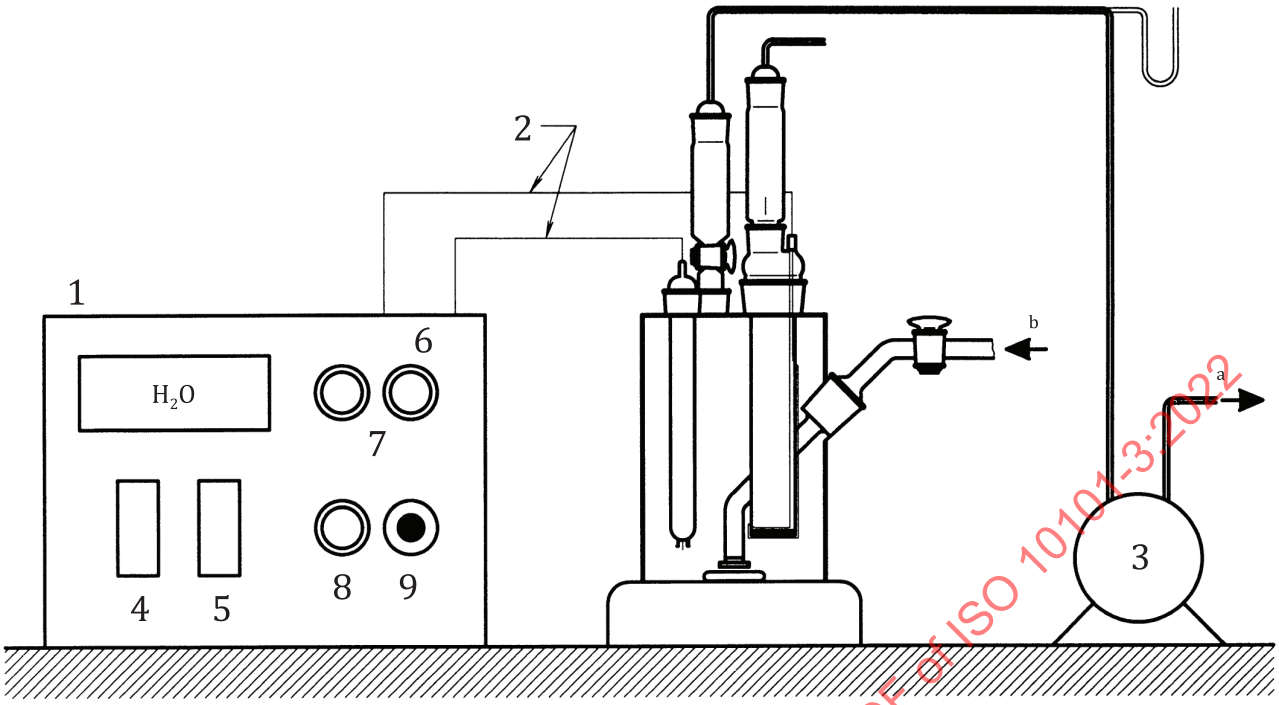
**6.1.3 Drying tube**, placed in the gas outlet line as in Figure 4.




**Key**

| | | | |
|---|---|---|---|
| 1 | magnetic stirrer | 6 | cathodic cell |
| 2 | anodic cell | 7 | cathode |
| 3 | platinum double electrode | 8 | diaphragm |
| 4 | drying tubes | 9 | anode |
| 5 | gas inlet | | |

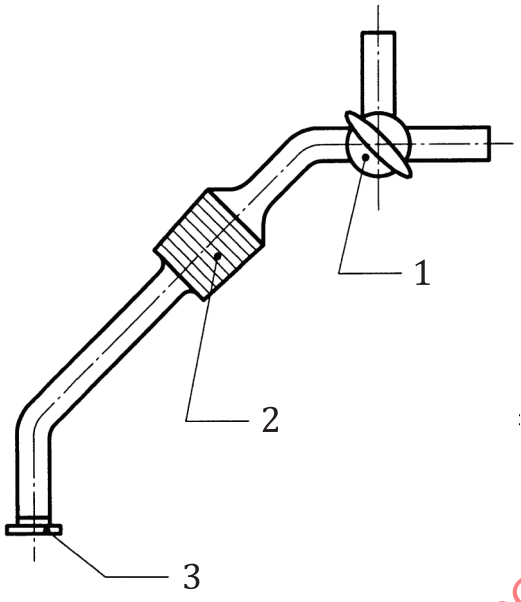
**Figure 1 — Titration cell**




**Key**

| | | | |
|---|---|---|---|
| 1 | controlling box | 6 | start/stop |
| 2 | electrical connections | 7 | optical cell indicator |
| 3 | gas meter | 8 | zero point |
| 4 | volt | 9 | on |
| 5 | ampere | | |
| a | Gas outlet. | b | Gas inlet. |

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



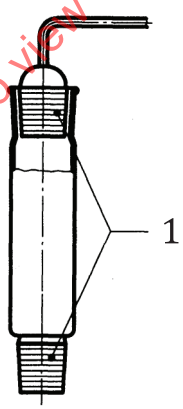

**Key**

1 3-way valve (e.g. ground tapes plug point)

2 normal glass with small holes

3 fritted glass or small holes are recommended

**Figure 3 — Gas inlet with 3-way valve**




**Key**

**1** conical ground joints

**Figure 4 — Drying tube in the gas outlet**



**6.2 Wet-test gas meter**, accurate to ±1 % of the volume passed, e.g. wet-test gas meter, Coriolis meter, etc.

**6.3 Syringe.**

## 7 Sampling

Follow the procedure as in ISO 10101-1.

All parts which come in 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 polyterafluoroethylene.

# 8 Procedure

## 8.1 Installation

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

## 8.2 Testing the response

Flush a syringe twice with reference solution (5.2). As soon as the measuring device is ready for measurement, use the syringe to inject a defined amount (about 10 µl) of reference solution 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 the 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.

If using a commercial reference solution contained in an ampoule, it should be handled according to the manufacturer's recommendations.

The results, expressed in micrograms, should agree with the mass of water introduced with the reference solution. It is acceptable if the deviation found does not exceed in the given limits stated by the producer.

NOTE If there is not a sufficiently good agreement with the recommendations given, look for a technical defect in the apparatus and resolve it before use.

## 8.3 Measurement

After switching on the measuring system, wait until the measuring cell has reached a state of equilibrium and a lowest-possible constant drift value has resulted.

To purge the inlet line, allow the measuring gas to pass via the 3-way valve into the outlet line or to atmosphere. Adjust the measuring gas flow rate to between 30 l/h and 40 l/h. 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.

When the measuring system is ready for measurement, the gas is passed through the measuring cell. The volume of gas passed is measured at the cell outlet. The volume of gas to be used depends on the anticipated concentration of water. When this volume has passed through the cell, return the 3-way valve to the former previous position. In addition to measuring the gas volume, measure the pressure and temperature of the measuring gas in the meter.

For very low water contents, the water measurement process can finish before the entire volume of gas has been added. This may be prevented by setting a wait or sampling period in the measuring device

## 8.4 Blank value determination

In the case of water concentrations (less than 100 mg/m$^3$), perform a blank value determination to correct for losses of iodine by evaporation during passage of the gas sample. To this end, install commercially available dry cartridges for example filled with phosphorus pentoxide (5.3) as close as it is possible to the inlet of the titration cell. Pass through an amount of dry gas, under the same