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

Part 1:
General requirements

Gaz naturel — Dosage de l'eau par la méthode de Karl Fischer —

Partie 1: Exigences générales

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Foreword

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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 10101-1:1993), which has been technically revised.

The main changes are as follows:

- Clause 2 and Bibliography were revised;
- New fixed structure numbering inserted.

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 method for the determination of moisture has several practical advantages compared to other methods for moisture determination, such as accuracy, speed and selectivity.

The Karl Fischer method is selective for water, because the titration reaction itself consumes water.

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.

KF titration is essentially based on the Bunsen reaction used for the determination of sulphur dioxide in aqueous solution:

$$2H_2O+SO_2+I_2 \rightarrow H_2SO_4+2HI$$

If an excess of sulphur dioxide with simultaneous neutralization of the sulphuric acid formed shift the reaction equilibrium to the right, the Bunsen reaction can also be used for the determination of water. Karl Fischer used pyridine as (neutralization) base, thus developing the classical KF reagent. This was a solution of iodine and sulphur dioxide in a solvent mixture of pyridine and methanol[9]. The fact that the pyridine contained in the reagent has a strong unpleasant odour and toxicity and the reaction runs stoichiometrically only within a certain pH range led to the revision of the KF reagents[9]. Scholz formulated the following KF reaction based on imidazole:

$$CH_3OH+SO_2+RN \rightarrow [RNH]SO_3CH_3$$

where RN = Base.

$$H_2O+I_2+[RNH]SO_3CH_3+2RN \rightarrow [RNH]SO_4CH_3+2[RNH]I$$

Volumetric KF titration is preferably used for the determination of large amounts of water in the range of 1 mg to 100 mg[10]. Coulometry, however, is a micro-method which is particularly well suited for determination of quantities of water from 10 µg to 10 mg[10]. In coulometric water determination, iodine is not added in the form of a titrating solution but rather directly produced from a iodine-containing solution by an anodic oxidation reaction[9]. 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.

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

Part 1:
General requirements

1 Scope

This document specifies general requirements for the determination of water in natural gas using the Karl Fischer method (see Reference [1]).

ISO 10101-2 and ISO 10101-3 specify two individual methods of determination, a titration procedure and a coulometric procedure, respectively.

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 10715, *Natural gas — Sampling guidelines*

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

4.1 General

Reaction of water present in the test sample with iodine and sulfur-dioxide in a methanol mixture (Karl Fischer reagent commercially available).

The oxidation of the alkylsulfite to alkylsulfate in reaction given by Formula (3) uses the water that theoretically is in the sample. Since water and iodine are used in a stoichiometric ratio 1:1, the quantity of water in the sample is calculated considering the iodine needed for the complete reaction. The iodine is measured by titration or by coulometry.

4.2 Principle of the titration method

A measured volume of gas is passed through a cell containing a relatively small volume of absorbent solution. Water in the gas is dissolved in the absorbent solution and subsequently titrated with Karl Fischer reagent, the endpoint being detected voltametrically, see ISO 10101-2.

4.3 Principle of the coulometric method

A measured volume of gas is passed through a cell containing anhydrous, previously titrated, anodic-solution, see ISO 10101-3. The iodine required for the titration of the dissolved water is coulometrically produced from the iodide present in the solution by Formula (1):

$$2I^- \rightarrow I_2 + 2e^- \tag{1}$$

5 Reactions and interferences

The following chemical reactions of water present in the test sample with iodine and sulfur-dioxide form the basis of this document:

$$ROH + SO_2 + RN \rightarrow [RNH]SO_3R \tag{2}$$

$$H_2O + I_2 + [RNH]SO_3CH_3 + 2RN \rightarrow [RNH]SO_4R + 2[RNH]I \tag{3}$$

where

ROH is an alcohol, typically methanol (or 2-methoxyethanol);

RN is a basic nitrogen compound.

Various gas components react with the Karl Fischer reagent and can give rise to erroneous results. Such components are oxidizing and reducing agents, e.g. hydrogen sulfide, mercaptans and certain basic nitrogenous substances.

Hydrogen sulfide and mercaptans are present in some natural gases. If their concentration is less than 20 % of the water content, interference due to their presence shall be corrected as follows:

$$\rho(H_2O)_a = \rho(H_2O) - \frac{9\rho_S(H_2S)}{16} - \frac{9\rho_S(RSH)}{32} \tag{4}$$

where

$\rho(H_2O)_a$ is the actual water content, in milligrams per cubic meter at 273,15 K (0 °C) and 101,325 kPa (1 atm);

$\rho(H_2O)$ is the observed or measured water content, in milligrams per cubic meter at 273,15 K (0 °C) and 101,325 kPa (1 atm);

$\rho_S(H_2S)$ is the measured sulfur as hydrogen sulfide, in milligrams per cubic meter at 273,15 K (0 °C) and 101,325 kPa (1 atm);

$\rho_S(RSH)$ is the measured sulfur as mercaptans in the gas, in milligrams per cubic meter at 273,15 K (0 °C) and 101,325 kPa (1 atm).

NOTE 1 The reaction mechanism of hydrogen sulfide and iodine was investigated by Xuting Zhi et al.[12]. They concluded that hydrogen sulfide and iodine might react with a stoichiometry of 1:2,5, not 1:1 as in aqueous solution. According to the statement above, the modification of hydrogen sulfide can be:

$$\frac{45\rho_S(H_2S)}{32} \tag{5}$$

At higher contents of H_2S and RSH Formula (4) is not applicable.

The sulfur present as hydrogen sulfide and mercaptans may be determined by gas chromatography (see ISO 19739) or by any other suitable method.

6 Sampling

Carry out sampling according to the general sampling guidelines given in ISO 10715. During sampling, ensure that the temperature of the gas stream is above the dew-point temperature. If necessary, the sampling equipment should be heated.

All parts in contact with the gas shall be of steel, glass or other suitable materials that do not alter the gas sample. The ends of pipes shall fit securely together, and the connecting pieces shall be made of fluoroelastomers.

7 Measurement uncertainty

Preferably the uncertainty of measurement results is estimated using data from interlaboratory comparisons (method validation studies) according to ISO 5725-2. Given such data, according to ISO 21748, the standard uncertainty is estimated by the reproducibility standard deviation for the concentration level concerned. Accordingly, the expanded uncertainty (k=2) is calculated as follows:

$$U = 2s_R \text{ or } U = {}^{R}\!/_{1,4}$$

Where S_R and R are the reproducibility standard deviation and the reproducibility limit for the concentration level concerned.

NOTE The repeatability standard deviation, s_r, is not a suitable uncertainty estimate, since it excludes major uncertainty contributions.

Alternatively, the uncertainty of measurement results may be estimated 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.

Bibliography

[1] ISO 760, *Determination of water — Karl Fischer method (General method)*

[2] ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

[3] ISO 10101-2, *Natural gas — Determination of water by the Karl Fischer method — Part 2: Volumetric procedure*

[4] ISO 10101-3, *Natural gas — Determination of water by the Karl Fischer method — Part 3: Coulometric procedure*

[5] ISO 19739, *Natural gas — Determination of sulfur compounds using gas chromatography*

[6] ISO 21748, *Guidance for the use of repeatability, reproducibility and trueness estimates in measurement uncertainty evaluation*

[7] ISO/IEC Guide 98-3, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

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