

INTERNATIONAL STANDARD

ISO
4317

Second edition
1991-08-01

Surface-active agents and detergents — Determination of water content — Karl Fischer method

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*Agents de surface et détergents — Détermination de la teneur en
eau — Méthode de Karl Fischer*

ISO 4317:1991

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Reference number
ISO 4317:1991(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 4317 was prepared by Technical Committee ISO/TC 91, *Surface active agents*.

This second edition cancels and replaces the first edition (ISO 4317:1977), of which it constitutes a technical revision.

Annexes A and B of this International Standard are for information only.

Surface-active agents and detergents — Determination of water content — Karl Fischer method

1 Scope

This International Standard specifies a method using Karl Fischer reagent for the determination of the water content of surface-active agents and detergents.

The method is applicable to products in the form of powders, pastes and solutions. For water contents of less than 1 % (*m/m*), it is the only method to be used.

It is applicable only if so indicated in the specific standard for each product.

As alkaline compounds react with Karl Fischer reagent, the method gives too high values in the case of samples containing alkali metal silicates, carbonates, hydroxides or borates. Therefore, samples shall be analysed for the presence of such alkali metal salts prior to the determination of the water content.

NOTE 1 A summary of a coulometric method is given in annex B for information.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard 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 607:1980, *Surface active agents and detergents — Methods of sample division*.

ISO 760:1978, *Determination of water — Karl Fischer method (General method)*.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*.

3 Definition

For the purposes of this International Standard, the following definition applies.

3.1 water content: The amount of free water, water of crystallization, absorbed water or occluded water, expressed as a percentage by mass, calculated from the amount of Karl Fischer reagent used in accordance with this International Standard.

4 Principle

Any water present in a test portion is reacted with a solution of iodine and sulfur dioxide in an appropriate mixture (Karl Fischer reagent), previously standardized by titration with an exactly known mass of water. The water content is calculated as a percentage by mass from the amount of reagent used.

5 Reagents

During the analysis, use only reagents of recognized analytical grade and only grade 2 distilled water (5.1).

5.1 Distilled water, or water of at least equivalent purity, complying with the requirements of ISO 3696 for grade 2.

5.2 Methanol, dry.

5.3 Karl Fischer reagent, preferably commercially prepared.

NOTE 2 A reagent containing pyridine may be prepared as described in annex A for information.

A non-pyridine reagent can be used if it has been shown to be suitable (to be included in the test report).

NOTE 3 A suitable non-pyridine-containing reagent is commercially available containing iodine, sulfur dioxide and an amine dissolved in 2-methoxyethanol.

5.4 Disodium tartrate dihydrate or **oxalic acid dihydrate**, to be used as the primary standard for the Karl Fischer reagent, or **water** (5.1).

5.5 Solvent, e.g. 2-methoxyethanol, propan-1-ol or methanol.

If it is known that these solvents interfere with the determination, e.g. for the determination of water in aldehydes or ketones, trichloromethane or dichloromethane may be used (if so, this shall be indicated in the test report).

WARNING — Trichloromethane and dichloromethane are harmful by inhalation and if swallowed, and irritating to the skin, with the risk of irreversible effects and the danger of serious damage to health in the event of prolonged exposure.

6 Apparatus

Ordinary laboratory apparatus and, in particular,

6.1 Karl Fischer apparatus, fully automatic or semi-automatic, consisting of:

- titrator with double platinum electrode;
- 20 ml piston burette;
- drying tubes containing activated silica gel, calcium chloride or magnesium perchlorate;
- titration vessel;
- magnetic stirring apparatus.

6.2 Micrometer syringe, capacity 100 μ l.

6.3 Graduated pipette, capacity 20 ml.

6.4 Syringe, nominal capacity about 10 ml, with a glass tube with an internal diameter of 2 mm to 4 mm, with a movable needle attached to the syringe by suitable means.

6.5 One-mark volumetric flask, capacity 100 ml.

7 Sampling

The laboratory sample of surface-active agent or detergent shall have been prepared and stored in accordance with the instructions given in ISO 607.

8 Procedure

Atmospheric moisture is the biggest source of interference in the Karl Fischer titration. Special attention shall be paid to thorough drying of the apparatus used and speedy handling of the test portions and solvents. For the method of use of the Karl Fischer apparatus, follow the manufacturer's instructions and ISO 760.

8.1 Determination of the water equivalent of the Karl Fischer reagent (5.3)

Determine the water equivalent of the reagent on each new container of reagent and then at least weekly.

It is necessary to check the titre of the Karl Fischer reagent, as the titre of the standard solutions is subject to change. The type of apparatus used and the desired analytical accuracy govern the frequency of such titre checks.

Place the magnetic stirring bar into the titration vessel of the Karl Fischer apparatus (6.1) using pincers, and transfer 10 ml of one of the solvents (5.5) used for the determination into the titration vessel and titrate with the Karl Fischer reagent (5.3).

In cases where it is absolutely necessary, e.g. the determination of water in aldehydes or ketones, use chloroform or dichloromethane (see 5.5) as solvent.

Either:

Weigh 200 mg to 250 mg of disodium tartrate dihydrate or oxalic acid dihydrate (5.4) in a weighing scoop to the nearest 0,1 mg. Transfer the tartrate or oxalic acid to the titration vessel and reweigh the weighing scoop. Dissolve the tartrate or oxalic acid in the solvent by gentle stirring.

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Or:

Introduce approximately 40 mg of water (5.1) from a dropping bottle, weighed before and after introducing the water into the titration vessel.

The amount of solvent used shall be such as to immerse the electrode by 2 mm to 3 mm.

Add Karl Fischer reagent until the electrometric end point has been reached. This is when, after addition of Karl Fischer reagent drop by drop, the observed value remains constant for 30 s.

The water equivalent $\rho(\text{H}_2\text{O})$, expressed in milligrams of water per millilitre, is given by one of the following equations:

$$\rho(\text{H}_2\text{O}) = \frac{m_1 \cdot w(\text{H}_2\text{O})}{100V_1}$$

or

$$\rho(\text{H}_2\text{O}) = \frac{m_2}{V_1}$$

where

m_1 is the mass, in milligrams, of disodium tartrate dihydrate or oxalic acid dihydrate (5.4) used;

m_2 is the mass, in milligrams, of water (5.1) used;

$w(\text{H}_2\text{O})$ is the water content, expressed as a percentage by mass, of the primary standard (5.4) used, i.e. 15,66 for sodium tartrate dihydrate or 28,57 for oxalic acid dihydrate;

V_1 is the volume, in millilitres, of Karl Fischer reagent (5.3) used in the titration.

8.2 Test portion

If the sample has a water content less than 1 % (m/m), use 5 g to 10 g (preferably to contain 10 mg to 50 mg water) of the laboratory sample (see clause 7), weighed to the nearest 1 mg.

If the sample has a water content higher than 1 % (m/m), prepare the test portion as follows:

Weigh, to the nearest 1 mg, 1 g to 5 g of the laboratory sample into the 100 ml volumetric flask (6.5). Add dry methanol (5.2) and dilute to the mark. Dissolve the water present in the sample by vigorous shaking. Insoluble salts will settle to the bottom when the solution is allowed to stand.

By means of the graduated pipette (6.3), take a volume of the supernatant methanolic solution corresponding to 10 mg to 50 mg of water.

NOTE 4 For some surface-active agents, for example zeolites, only part of the water of crystallization will be determined by the method described.

8.3 Determination of the water content

Place 20 ml of solvent (5.5) and the magnetic stirring bar (using pincers) in the titration vessel of the Karl Fischer apparatus (6.1). Whilst stirring, add Karl Fischer reagent (5.3) until the end point is reached as indicated by the instrument reading. Do not record the amount of reagent used.

Add the test portion (see 8.2). Stir to dissolve, and titrate to the same end point. Record the volume of Karl Fischer reagent used.

Carry out a second determination by adding another test portion and repeating the titration.

9 Expression of results

The water content of the product, expressed as a percentage by mass, is given by the formula:

$$\frac{\rho(\text{H}_2\text{O}) \cdot V_2}{m_0} \times 100$$

where

V_2 is the volume, in millilitres, of Karl Fischer reagent (5.3) used for the determination (see 8.3);

m_0 is the mass, in milligrams, of the test portion (see 8.2);

$\rho(\text{H}_2\text{O})$ is as defined in 8.1.

10 Precision

10.1 Repeatability

The difference between the results of two determinations carried out simultaneously or in rapid succession by the same operator on the same sample should not be greater than 6 % relative.

10.2 Reproducibility

The difference between two results obtained in different laboratories on portions of the same sample should not be greater than 10 % relative.

11 Test report

The test report shall include the following particulars:

- a) all information necessary for the complete identification of the sample;
- b) a reference to this International Standard and the type of solvent and of Karl Fischer reagent used;
- c) the results obtained and the units in which they have been expressed;
- d) the test conditions;
- e) any operational details not specified in this International Standard or in the International Standards to which reference is made, as well as any operational details regarded as optional, plus details of any incidents likely to have affected the results.

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Annex A (informative)

Preparation of Karl Fischer reagent containing pyridine

Place 670 ml of methanol or 2-methoxyethanol (5.5) in a dry brown-glass flask, of capacity 1 litre, fitted with a ground-glass stopper.

Add about 85 g of iodine. Stopper the flask and shake it occasionally until the iodine is completely dissolved. Then add approximately 270 ml of pyridine containing not more than 500 mg of water per kilogram, stopper the flask again and mix thoroughly. As the reaction will be exothermic, maintain the flask at about 0 °C, for example by immersing it in an ice bath. Using the method described below, dissolve 65 g of sulfur dioxide in this solution, ensuring that the temperature of the liquid does not exceed 20 °C.

Replace the ground-glass stopper by an attachment for introducing sulfur dioxide (consisting of a cork with a thermometer and a glass inlet tube passing through it, thermometer and inlet tube reaching to within 10 mm of the bottom of the flask) and a small capillary tube for connecting to the atmosphere.

Place the whole assembly with the cooling bath on a balance and weigh to the nearest 1 g. Then connect the inlet tube to a cylinder of sulfur dioxide by means of a flexible connection and a drying tube filled with drying agent and gently open the tap on the cylinder.

Adjust the rate of flow of sulfur dioxide so that all the gas is absorbed but the liquid does not rise up the inlet tube.

Then maintain the balance in equilibrium by gradually increasing the tare, and ensure that the temperature of the liquid does not rise above 20 °C. Close the tap on the cylinder as soon as the increase in mass reaches 65 g.

Immediately remove the flexible connection and reweigh the flask with the ice bath and inlet tube. The mass of dissolved sulfur dioxide should be between 60 g (minimum) and 70 g. A slight excess is not serious.

Stopper the flask, mix the solution and leave for at least 24 h before using it (as the result of imperfectly understood reactions which occur in the fresh reagent, the water equivalent of the reagent decreases rapidly to begin with and then much more slowly).

This water equivalent shall be between 3,5 mg/ml and 4,5 mg/ml. It shall be determined daily if methanol has been used, but may be determined less frequently if 2-methoxyethanol has been used.

It is possible to prepare Karl Fischer reagent having a lower water content by diluting the solution prepared as described above with dry methanol (5.2).

Store the reagent in the dark and protect from atmospheric moisture. It should preferably be stored in the reagent bottle of the Karl Fischer apparatus (6.1).

Annex B
(informative)

Summary of the coulometric method

In the coulometric variation of the Karl Fischer determination of water, the iodine necessary for the reaction with water is produced by the anodic oxidation of iodide.

The amount of iodine produced is proportional to the quantity of electricity consumed, the unit of which is the coulomb.

The commercial instruments which have been developed to make use of this principle are sophisticated, usually being fully automatic and computerized. An instrument contains two cells, an anodic and a cathodic, separated by a membrane

and containing electrolytes, into which platinum electrodes dip. The reaction takes place in the anodic cell. The rest of the instrument facilitates the reaction, the measurement of the number of coulombs of electricity consumed and its conversion into the corresponding quantity of water.

The coulometric method is more sensitive than the titrimetric method and permits the determination of smaller amounts of water. It is also sensitive to atmospheric moisture and chemical side reactions, however. It cannot be relied on for arbitration or referee purposes.

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