Surface active agents — Determination of water content — Karl Fischer method

The European Standard EN 13267:2001 has the status of a British Standard

ICS 71.100.40

National foreword

This British Standard is the official English language version of EN 13267:2001. It supersedes BS 6829-1.5:1990 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee CII/34, Methods of test for surface active agents, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this committee can be obtained on request to its secretary.

Additional information

Some textual errors were discovered when the English language version of EN 13267:2001 was adopted as the national standard. Some of the chemical names are not consistently presented and do not conform to IUPAC recommendations. These textual errors have been reported to CEN in a proposal to amend the text of the European Standard.

Cross-references

The British Standards which implement international or European publications may be found in the BSI Standards Catalogue under the section entitled “International Standards Correspondence Index”, or by using the “Find” facility of the BSI Standards Electronic Catalogue.

This British Standard, having been prepared under the direction of the Sector Committee for Materials and Chemicals, was published under the authority of the Standards Committee and comes into effect on 15 June 2001

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English version

Surface active agents — Determination of water content — Karl Fischer method

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

Grenzflächenaktive Stoffe — Bestimmung des Wassergehaltes — Verfahren nach Karl Fischer

This European Standard was approved by CEN on 4 February 2001.

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EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

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Contents

Foreword

This European Standard has been prepared by Technical Committee CEN/TC 276, Surface active agents, the Secretariat of which is held by AFNOR.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by September 2001, and conflicting national standards shall be withdrawn at the latest by September 2001.

The annexes A and B are informative.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This European Standard specifies the Karl Fischer method using electrometric end point detection for the determination of the water content of surface active agents.

The method is applicable to products in form of powders, pastes and solutions.

The following substances interfere with Karl Fischer reagent: alkali metal silicates, carbonates; hydroxides and borates; oxidizing agents, ketones, aldehydes; strong mineral acids and strong bases. Samples that contain any of these substances cannot be measured directly by this present method; in those situations the solvent system and/or the Karl Fischer reagent have to be modified, but these modifications are out of the scope of this European Standard.

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

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

ISO 607, *Surface active agents and detergents — Methods of sample division*.

3 Terms and definitions

For the purposes of this European Standard, the following terms and definitions apply.

3.1
water content
amount of water, water of cristallization, absorbed water or occluded water, expressed as a percent by mass

4 Principle

The water present in the 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 from the amount of reagent used as percent by mass.

5 Reagents

During the analysis, use only reagents of recognized analytical grade and water complying with grade 1 as defined in EN ISO 3696.

5.1 **Solvent**, methanol, 2-methoxyethanol or propan-1-ol

NOTE The water content should be as low as possible in order to save Karl Fischer reagent.

5.2 **Karl Fischer reagent**, having a water equivalent of approximately 5 mg/ml, preferably commercially prepared.

NOTE A non-pyridine containing reagent is preferred mainly for safety reasons. A commercially available reagent containing iodine, sulfur dioxide and an amine dissolved in 2-methoxyethanol is suitable. A pyridine reagent can be used if it has been shown to be suitable. This should be included in the test report. A reagent containing pyridine can be prepared as specified in annex A.

6 Apparatus

Ordinary laboratory apparatus and the following:

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

- titrator with double platinum electrode;
- piston burette, with a resolution less or equal to 0,01 ml; capable of controlling the dosage rate, the time of delay, the stop time and the drift;
- drying tubes containing molecular sieve pore size 0,3 nm (silica gel is not sufficient as a protective agent);
- magnetic stirrer.

6.2 Gas tight syringe, capacity 100 µl (optional).

6.3 Clinical glass syringe, with movable needle.

6.4 Analytical balance, accurate to 0,1 mg.

7 Sampling

The laboratory sample shall have been prepared and stored in accordance with ISO 607.

8 Procedure

8.1 General

Atmospheric moisture is the biggest source of interference in the Karl Fischer titration. Take care to dry the apparatus thoroughly and to handle the test portions and solvents speedily to prevent access of moisture. Operate the Karl Fischer apparatus in accordance with the manufacturer’s instructions.

8.2 Determination of the water equivalent of the Karl Fischer reagent

8.2.1 General

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

NOTE The water equivalent can change during storage. The type of apparatus used and the desired analytical accuracy govern the frequency of determination of the water equivalent.

8.2.2 Preparation

Clean the electrode with tissue paper moistened with a suitable solvent, e.g. acetone. Wipe-off the acetone. Install a clean and dry titration vessel; introduce a clean and dry magnetic stirring bar.

Transfer enough volume of solvent (5.1) as to immerse the electrode platinum tips by 2 mm to 3 mm.

Titrate with the Karl Fischer reagent (5.2) in order to neutralize any trace of moisture, avoiding any excess of reagent.

NOTE If an automatic apparatus is used, the following instrumental conditions are recommended:

— maximum dosage rate	15 ml/min;

— minimum increment	9 µl;
— initial volume	0 ml;
— stop time	20 s;
— initial delay	10 s;
— drift control	automatically.

8.2.3 Determination

Introduce a precise amount of water as to consume a volume of Karl Fischer reagent corresponding to more than 80 % of the capacity of the piston burette. The water shall be introduced using the syringe (6.2); record the exact amount of water (m_w) introduced by weighing the syringe to the nearest 0,1 mg before and after introducing the water.

NOTE A digital syringe can also be used to control the amount of water added as long as there is enough evidence that its accuracy is at least equal to that of the analytical balance (6.4).

Titrate with Karl Fischer reagent (5.2) until the electrometric end point has been reached (see 8.2.2 note).

8.2.4 Calculation

The water equivalent E_w, expressed as milligrams of water per millilitre, is given by the equation (1):

$$E_\mathrm{w} = \frac{m_\mathrm{w}}{V_1} \qquad (1)$$

where:

m_w is the mass, in milligrams, of water introduced;

V_1 is the volume, in millilitres, of Karl Fischer reagent consumed at the titration.

Repeat the introduction of water and titration two more times. Calculate the mean of these E_w values for which standard deviation shall be less than 0,05 mg/ml. Retain this mean as the water equivalent E_w.

8.3 Determination of the water content

8.3.1 General

Depending on the characteristics of the laboratory sample, one of the following two methods shall be chosen, namely the general method (8.3.2) or the dissolution method (8.3.3).

The general method is suitable for samples which are homogeneous and easy to dispense into the titration vessel.

The dissolution method shall be used for samples for which homogeneity is questionable and/or that are difficult to dispense into the titration vessel.

8.3.2 General method

8.3.2.1 Preparation

Proceed as described in 8.2.2.

If the titration vessel contains too much solvent from previous determinations, remove some of it. Also be aware of solid deposits on platinum tips of the electrode, which can cause important errors; remove them with a suitable solvent and tissue paper.

8.3.2.2 Determination

Fill into the titration vessel a test portion (m) of the material whose percentage of water is to be determined. Check the amount to the nearest 0,1 mg by difference of masses. Chose the amount as to consume a volume of Karl Fischer reagent corresponding to more than 50 % of the capacity of the piston burette.

Titrate with Karl Fischer reagent (5.2) until the electrometric end point has been reached (see 8.2.2 note).

8.3.2.3 Calculation

The water content W_{H_20}, expressed as percent by mass, in the sample is given by the equation (2):

$$W_{H_2 0} = \frac{V_2 \times E_w}{m \times 10} \tag{2}$$

where:

m is the mass, in grams, of the test portion taken in 8.3.2.2;

E_w is the water equivalent of Karl Fischer reagent according to 8.2.4;

V_2 is the volume, in millilitres, of Karl Fischer reagent consumed in 8.3.2.2.

8.3.3 Dissolution method

8.3.3.1 Determination

Weigh a suitable amount of laboratory sample (m_1) into a dry flask. Add a suitable amount of any organic solvent (m_2) that does not interfere with Karl Fischer reagent (5.2). The amounts of sample and solvent shall be chosen as to use the maximum possible amount of sample and the minimum proportion of the solvent, in order to obtain a manageable blend and not compromise the representativity of the sample uptake. Record the mass to the nearest 0,001 g. Stopper the flask and shake until a homogeneous blend is obtained.

If at this stage insoluble salts settle in the bottom of the flask, the method has to be abandoned, because:

a) part of the water might have been removed by the insoluble salts as crystallization water; and

b) a rigorous procedure would have to involve the correct determination of the mass of the insoluble salts.

Determine the water content of both the solvent and the blend, following the procedure given in 8.3.2.

8.3.3.2 Calculation

The water content $W_{H_2 0}$, expressed in percent by mass, in the sample is given by the equation (3):

$$W_{H_2 0} = \frac{W_b \left(m_1 + m_2\right) - m_2 \times W_2}{m_1} \qquad (3)$$

where:

m_1	is the mass, in grams, of sample taken in 8.3.3.1;
m_2	is the mass, in grams, of solvent used in 8.3.3.1;
W_b	is the water content in the blend according to 8.3.3.1, in percent (m/m);
W_2	is the water content in the solvent according to 8.3.3.1, in percent (m/m).

9 Precision

9.1 Repeatability limit

The absolute difference between two independent single test results, obtained using the same method on identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, will not exceed the repeatability limit, r, in more than 5 % of cases.

According to the ring test results given in annex B, the repeatability limit, r, shall be:

- less than or equal to 0,005 g/100 g for a water content of approximately 0,07 % (m/m); or
- less than or equal to 0,3 g/100 g for a water content of approximately 12,2 % (m/m); or
- less than or equal to 0,46 g/100 g for a water content of approximately 65,8 % (m/m).

9.2 Reproducibility limit

The absolute difference between two independent single test results, obtained using the same method on identical test material in different laboratories by different operators using different equipment, will not exceed the reproducibility limit, R, in more than 5 % of cases.

According to the ring test results given in annex B, the reproducibility limit, R, shall be:

- less than or equal to 0,02 g/100 g for a water content of approximately 0,07 % (m/m); or
- less than or equal to 0,6 g/100 g for a water content of approximately 12,2 % (m/m); or
- less than or equal to 2,9 g/100 g for a water content of approximately 65,8 % (m/m).

10 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 European Standard and to the method used (general or dissolution method);

c) the result;

d) details of any operation not specified in this European Standard and any operation regarded as optional as well as any incidents likely to have affected the results.

Annex A
(informative)

Preparation of Karl Fischer reagent containing pyridine

Place 670 ml of methanol or 2-methoxyethanol (5.2) in a dry brown-glass flask, with a capacity of 1 l, 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/kg of water, stopper the flask again and mix thoroughly. As the reaction will be exothermic, keep 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 keep 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 re-weigh 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 in the beginning 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 can be determined less frequently by using 2-methoxyethanol.

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

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

Annex B
(informative)

Interlaboratory test results

These statistical data were obtained by a ring test carried out by CESIO/AIS WG “Analysis” in 1995 on three samples. The evaluation was performed in accordance with ISO 5725-2:

Table B.1 — Samples and methods used

Sample	Description	Method used
A	Commercial ethoxylated (2 EO) $C_{12}C_{14}$ fatty alcohol	General (8.3.2)
B	Distearyldimethylammonium chloride	Dissolution (8.3.3)
C	Alkylamidopropylbetaine	General (8.3.2)

Table B.2 — Precision data

Designation	Sample A	Sample B	Sample C
Number of laboratories participating	13	13	13
Number of laboratories not eliminated	11	12	13
Number of individual values of all laboratories	22	24	26
Mean value (g/100 g)	0,07	12,2	65,8
Repeatability standard deviation s_r (g/100 g)	0,002	0,15	0,17
Repeatability limit r: $r = (2,8 \times s_r)$ (g/100 g)	0,005	0,42	0,47
Coefficient of variation repeatability V_r (%)	2,9	1,2	0,26
Reproducibility standard deviation s_R (g/100 g)	0,007	0,21	1,05
Reproducibility limit R: $R = (2,8 \times s_R)$ (g/100 g)	0,021	0,59	2,94
Coefficient of variation reproducibility V_R (%)	10	1,7	1,6

Bibliography

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.*

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