INTERNATIONAL STANDARD ISO 760

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Determination of water — Karl Fischer method (General method)

Dosage de l'eau — Méthode de Karl Fischer (Méthode générale)

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up 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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

Prior to 1972, the results of the work of the technical committees were published as ISO Recommendations; those documents have subsequently been transformed into International Standards. As part of that process, Technical Committee ISO/TC 47, reviewed ISO Recommendation R 760-9168 and found it technically suitable for transformation. International Standard ISO 760-1978 therefore replaced ISO Recommendation R 760-1968.

ISO Recommendation R 760-1968 had been approved by the member bodies of the following countries :

Australia
Austria
Belgium
Chile
Colombia
Czechoslovakia
Egypt, Arab Rep. of
France
Germany, F.R.
Hungary
India
Israel
Italy
Japan
Korea, Rep. of
Netherlands
Poland
Portugal
Romania
Spain
United Kingdom
U.S.S.R.
Yugoslavia

The member bodies of the following countries had expressed disapproval of the Recommendation on technical grounds :

New Zealand
U.S.A.

The member body of the following country disapproved the transformation of ISO/R 760 into an International Standard :

Netherlands

Printed in Switzerland

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INTERNATIONAL STANDARD **ISO 760-1978 (E)**

Determination of water – Karl Fischer method (General method)

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a general method known as the Karl Fischer method[1], suitable for the determination of free water or water of crystallization in most solid or liquid chemical products, both organic and inorganic.

Precautions are necessary in certain cases and these are specified in the appropriate International Standards.

Two methods of titration, depending on whether the end-point is detected visually or electrometrically, are specified. The visual method can be used when no electrometric apparatus is available but is applicable only to colourless solutions; it is always a direct titration. The electrometric method, on the other hand, may involve either a direct titration or a back-titration. The electrometric method, whether by direct titration or back-titration, is the more accurate, and for this reason is recommended.

2 PRINCIPLE

Reaction of any water present in a test portion with a solution of iodine and sulphur dioxide in a pyridine/methanol mixture (Karl Fischer reagent), previously standardized by titration with an exactly known mass of water (see 6.1, 7.1 and 8.1).

NOTE – Methanol may be replaced by 2-methoxyethanol (ethylene glycol monomethyl ether). With this solvent, a more constant titration volume is obtained and the reagent can be used with aldehydes and ketones, without using any special technique.[2]

3 REACTIONS[3]

$$H_2O + I_2 + SO_2 + 3\,C_5H_5N \rightarrow 2\,C_5H_5N.HI + C_5H_5N.SO_3$$

$$C_5H_5N.SO_3 + ROH \rightarrow C_5H_5NH.OSO_2\,OR$$

4 REAGENTS AND MATERIALS

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Methanol, not containing more than 0,05 % (*m/m*) of water. If the reagent contains more than this quantity of water, dry it by distillation from magnesium turnings activated with iodine. Collect the distillate in a receiver protected from atmospheric moisture by means of a guard tube filled with the desiccant (4.9).

4.2 2-Methoxyethanol (Ethylene glycol monomethyl ether), not containing more than 0,05 % (*m/m*) of water. If the reagent contains more than this quantity of water, dry it by distillation, rejecting the first portion of distillate, which contains the water.

4.3 Pyridine, not containing more than 0,05 % (*m/m*) of water. If the reagent contains more than this quantity of water, dry it by distillation, rejecting the first portion of distillate, which contains the water.

4.4 Sample solvent : either a mixture containing 4 parts by volume of the methanol (4.1) and 1 part by volume of the pyridine (4.3), or (preferably for determinations with compounds containing carbonyl groups) a mixture containing 4 parts by volume of the 2-methoxyethanol (4.2) and 1 part by volume of the pyridine (4.3). In special cases, other solvents may be recommended, for example acetic acid, pyridine or a mixture containing 1 part by volume of the methanol (4.1) and 3 parts by volume of chloroform.

4.5 Karl Fischer reagent

Place 670 ml of the methanol (4.1) or the 2-methoxyethanol (4.2) in a dry brown glass flask, fitted with a ground glass stopper and having a capacity slightly greater than 1 litre.

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 the pyridine (4.3), stopper the flask again and mix thoroughly. Using the method described below, dissolve 65 g of sulphur dioxide in this solution, cooling to ensure that the temperature of the liquid does not exceed 20 °C.

NOTE – As the reaction is exothermic, it is necessary to cool the flask from the beginning and to maintain it at about 0 °C, for example by immersing it in an ice bath or in crushed solid carbon dioxide.

Replace the ground glass stopper by an attachment for introducing sulphur dioxide, consisting of a cork bearing a thermometer and a glass inlet tube 6 mm × 8 mm, 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 ice bath on a balance and weigh to the nearest 1 g. Connect the inlet tube to a cylinder of sulphur dioxide by means of a flexible connection and a drying tube filled with the desiccant (4.9) and gently open the tap on the cylinder.

Adjust the rate of flow of sulphur dioxide so that all the gas is absorbed without the liquid showing any sign of rising in the inlet tube.

Maintain the equilibrium of the balance 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 and its inlet attachment. The mass of dissolved sulphur dioxide should be between 60 and 70 g. A slight excess is not harmful.

Stopper the flask, mix the solution and leave for at least 24 h before using it. In fact, 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 is between 3,5 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 the sample solvent (4.4).

Store the reagent in the dark and protected from atmospheric moisture. It should preferably be stored in the reagent bottle (5.1.1.5).

4.6 Sodium tartrate dihydrate ($Na_2C_4H_4O_6.2H_2O$), or **water.**

4.7 Water/methanol, standard solution corresponding to 10 g of water per litre.

Using a microburette or a pipette, place 1 ml of water in a perfectly dry 100 ml one-mark volumetric flask containing approximately 50 ml of the methanol (4.1). Dilute to the mark with the methanol and mix. [For standardization of the Karl Fischer reagent (4.5) with this solution, see annex A, clause A.1 or A.2, depending on whether the visual method or the direct electrometric method is used.]

1 ml of this standard solution contains 10 mg of water.

4.8 Water/methanol, standard solution corresponding to 2 g of water per litre.

Using a microburette or a pipette, place 1 ml of water in a perfectly dry 500 ml one-mark volumetric flask containing approximately 100 ml of the methanol (4.1). Dilute to the mark with the same methanol and mix. (See the correspondence by volume of this solution with the Karl Fischer reagent in 8.2.2.)

1 ml of this standard solution contains 2 mg of water.

4.9 Aluminium sodium silicate, anhydrous, in the form of granules of diameter 1,7 mm, for use as a desiccant. The granules may be regenerated by washing with water and drying at 350 °C for at least 48 h.

Alternatively, **activated silica gel** may be used as a desiccant.

4.10 Silicone-base grease, for lubricating the ground glass joints.

5 APPARATUS

All the glassware used shall be previously dried for 30 min in an oven controlled at approximately 130 °C, then allowed to cool and stored in a desiccator containing the desiccant (4.9).

5.1 For direct titration (by visual method or electrometric method)

5.1.1 A suitable form of apparatus for this method is given in annex B, should no commercial apparatus be available. This standard apparatus comprises the parts described below.

5.1.1.1 Automatic burette, of capacity 25 ml, with a fine point, graduated in 0,05 ml and protected from atmospheric moisture by a guard tube filled with the desiccant (4.9).

5.1.1.2 Titration vessel, of effective capacity 100 ml, connected to the tap of the automatic burette (5.1.1.1) by a ground glass joint and having two side tubes, one permitting the introduction of platinum electrodes if the electrometric method is used and the other fitted with a "vaccine cap" to permit the introduction of liquid test portions by means of a syringe without opening the vessel.

5.1.1.3 Platinum electrodes (see figures 1 and 2, annex B), fused to a glass tube enabling them to be introduced into the bottom of the titration vessel (5.1.1.2) and joined to two copper wires which in turn are connected to the device for the electrometric detection of the end-point (5.1.1.7). (These are omitted in the case of the visual method.)

5.1.1.4 Electromagnetic stirrer, operating at a rotational frequency of 150 to 300 min^{-1}, with a mild steel bar coated with glass or polytetrafluorethylene (PTFE), and fixed on a base of adjustable height.

5.1.1.5 Reagent bottle for the Karl Fischer reagent, of capacity approximately 3 litres, of brown glass, in which the filling tube of the automatic burette (5.1.1.1) is immersed through the ground glass stopper.

5.1.1.6 Rubber bulb, connected to a Drechsel bottle filled with the desiccant (4.9), for the admission of dry air under pressure into the reagent bottle (5.1.1.5) in order to fill the automatic burette (5.1.1.1).

5.1.1.7 Device for the electrometric detection of the end-point, shown diagramatically in figure 3, annex B. (This is omitted in the case of the visual method.)

5.1.2 Medical syringes, of suitable capacity, the volume of which is calibrated.

5.1.3 Small glass tube, closed at one end and fitted at the other with a rubber stopper, used for weighing and introducing into the titration vessel, for example, the mass of sodium tartrate (4.6) (approximately 0,250 g) used to standardize the Karl Fischer reagent (4.5), or possibly test portions of solid products.

5.2 For electrometric back-titration method

5.2.1 A suitable form of apparatus for this method is given in annex C, should no commercial apparatus be available. This standard apparatus comprises the parts described below.

5.2.1.1 Two automatic burettes, of capacity 25 ml, with fine points, connected directly to their filling containers, one of brown glass for the Karl Fischer reagent (4.5) and the other for the standard water/methanol solution (4.8).

5.2.1.2 Titration vessel, of effective capacity 100 ml, connected to the automatic burettes (5.2.1.1) by means of ground glass joints and having two side tubes, one permitting the introduction of platinum electrodes and the other fitted with a "vaccine cap" to permit the introduction of liquid test portions by means of a syringe without opening the vessel.

5.2.1.3 Drying tube, connecting the filling containers of the burettes (5.2.1.1) and the stopper of the titration vessel (5.2.1.2) by a closed circuit.

5.2.1.4 Platinum electrodes (see figures 4 and 5, annex C), fused to a glass tube enabling them to be introduced into the bottom of the titration vessel (5.1.1.2) and joined to two copper wires which in turn are connected to the device for the electrometric detection of the end-point (5.2.1.6).

5.2.1.5 Electromagnetic stirrer, operating at a rotational frequency of 150 to 300 min^{-1}, with a mild steel bar coated with glass or polytetrafluorethylene (PTFE), and fixed on a base of adjustable height.

5.2.1.6 Device for the electrometric detection of the end-point, shown diagrammatically in figure 3, annex B.

5.2.2 Medical syringes, of suitable capacity, the volume of which is calibrated.

5.2.3 Small glass tube, closed at one end and fitted at the other with a rubber stopper, used for weighing and introducing into the titration vessel, for example, the mass of sodium tartrate (4.6) (approximately 0,250 g) used to standardize the Karl Fischer reagent (4.5), or possibly test portions of solid products.

6 VISUAL TITRATION

6.1 Principle for the detection of the end-point

Development of colour in the test portion by addition of the first drop of excess Karl Fischer reagent, coloured with iodine which gradually becomes colourless on addition to the test portion containing the water to be determined.

6.2 Procedure

6.2.1 *Standardization of the Karl Fischer reagent*

6.2.1.1 Assemble the apparatus as shown in annex B, lubricating the joints with the grease (4.10). Introduce by means of a syringe (5.1.2) 25 ml of the methanol (4.1) into the titration vessel (5.1.1.2) through the "vaccine cap". Switch on the electromagnetic stirrer (5.1.1.4). In order to cause reaction of the traces of water present in the methanol, add the Karl Fischer reagent (4.5) from the automatic burette (5.1.1.1) until a brown colour is obtained.

6.2.1.2 In the small glass tube (5.1.3), weigh, to the nearest 0,000 1 g, approximately 0,250 g of the sodium tartrate (4.6). Place this in the titration vessel very quickly, removing the "vaccine cap" for a few seconds, then weigh the small glass tube, so as to determine, by difference, the mass (m_1) of the sodium tartrate used.

Standardization may also be effected by introducing a mass (m_2) of water of approximately 0,040 g from a dropping bottle, weighed before and after introduction into the titration vessel.[1]

Titrate the known quantity of water introduced with the Karl Fischer reagent (4.5) to be standardized, until the same brown colour as in 6.2.1.1 is obtained, and note the volume (V_1) of reagent used.

6.2.2 *Determination*

Empty the titration vessel (5.1.1.2) by means of its drain tap. Place in it 25 ml (or the volume specified in the procedure for the product to be analysed) of the methanol (4.1) or other solvent (4.3 or 4.4), using a syringe (5.1.2) passing through the "vaccine cap". Switch on the electromagnetic stirrer (5.1.1.4). In order to cause reaction of the traces of water present in the methanol, add the Karl Fischer reagent (4.5) from the automatic burette (5.1.1.1) until a brown colour is obtained.

Introduce the specified test portion by means of a syringe in the case of a liquid, or weighed to the nearest 0,000 1 g

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[1] For standardization with the standard water/methanol solution (4.7), see annex A, clause A.1.

in the small glass tube (5.1.3) in the case of a solid powder. Titrate with the Karl Fischer reagent until the same brown colour is obtained.

Note the volume (V_2) of Karl Fischer reagent used for the determination.

NOTE — It is advisable to use a test portion such that its water content corresponds to a volume of Karl Fischer reagent that can be measured with sufficient accuracy. If necessary, increase in proportion the quantities of solvent and test sample used and then use a titration vessel of suitable capacity.

6.3 Expression of results

6.3.1 *Water equivalent of the Karl Fischer reagent*

The water equivalent T of the Karl Fischer reagent (4.5), expressed in milligrams of water per millilitre of reagent, is given by the formula

$$T = \frac{m_1 \times 0{,}156\,6}{V_1} \text{ or } T = \frac{m_2}{V_1}$$

where

m_1 is the mass, in milligrams, of the sodium tartrate (4.6) introduced if this reagent is used for the standardization (6.2.1.2);

m_2 is the mass, in milligrams, of water introduced if pure water is used for the standardization (6.2.1.2);

V_1 is the volume, in millilitres, of the Karl Fischer reagent (4.5) used for the standardization;

0,156 6 is the factor for calculation of the water of the sodium tartrate dihydrate.

6.3.2 *Water content of the sample*

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

$$\frac{V_2 \times T}{m_0 \times 10} \text{ or } \frac{V_2 \times T}{V_0 \times \rho \times 10}$$

where

m_0 is the mass, in grams, of the test portion (in the case of solid products);

V_0 is the volume, in millilitres, of the test portion (in the case of liquid products);

ρ is the density of the sample, in grams per millilitre, at 20 °C (in the case of liquid products);

V_2 is the volume, in millilitres, of the Karl Fischer reagent (4.5) used for the determination (6.2.2);

T is the water equivalent, in milligrams per millilitre, of the Karl Fischer reagent, calculated in accordance with 6.3.1.

7 DIRECT ELECTROMETRIC TITRATION

7.1 Principle for the detection of the end-point

Immersion in the solution of two platinum electrodes subjected to a potential difference : while water is present in the solution, the polarization of the cathode opposes the passage of a current. Indication of the end-point of the titration by the depolarization of the cathode accompanied by a sudden increase in current (which is shown by a suitable electrical device).

7.2 Procedure

7.2.1 *Standardization of the Karl Fischer reagent*

7.2.1.1 Assemble the apparatus as shown in figure 1, annex B, lubricating the joints with the grease (4.10). Introduce by means of a syringe (5.1.2) 25 ml of the methanol (4.1) into the titration vessel (5.1.1.2) through the "vaccine cap". Switch on the electromagnetic stirrer (5.1.1.4) and close the circuit of the device for the electrometric detection of the end-point (5.1.1.7).

Adjust the apparatus so that a potential difference of 1 to 2 V is applied to the electrodes and the galvanometer shows a low current, usually a few microamperes. In order to cause reaction of the traces of water present in the methanol, add the Karl Fischer reagent (4.5) until the galvanometer shows a sudden increase in current of about 10 to 20 µA, which remains stable for at least 1 min.

7.2.1.2 In the small glass tube (5.1.3), weigh, to the nearest 0,000 1 g, approximately 0,250 g of the sodium tartrate (4.6). Place this in the titration vessel very quickly, removing the "vaccine cap" for a few seconds; then weigh the small glass tube, so as to determine, by difference, the mass (m_3) of the sodium tartrate used.

Standardization may also be effected by introducing a mass (m_4) of water of approximately 0,040 g from a dropping bottle, weighed before and after introduction into the titration vessel.[1]

Titrate the known quantity of water introduced with the Karl Fischer reagent (4.5) to be standardized, until the same deflection of the pointer of the galvanometer is reached and remains stable for at least 1 min. Note the volume (V_3) of reagent used.

7.2.2 *Determination*

Empty the titration vessel (5.2.1.2) by means of its drain tap. Place in it 25 ml (or the volume specified in the pro-

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[1] For standardization with the standard water/methanol solution (4.7), see annex A, clause A.2.

cedure for the product to be analysed) of the methanol (4.1) or other solvent (4.3 or 4.4), using a syringe (5.1.2) passing through the "vaccine cap". Switch on the electromagnetic stirrer (5.1.1.4). In order to cause reaction of the traces of water present in the solvent used, add the Karl Fischer reagent (4.5), proceeding as specified in 7.2.1 until there is a sudden and constant deflection lasting for at least 1 min.

Introduce the specified test portion by means of a syringe in the case of a liquid or weighed to the nearest 0,000 1 g in a small glass tube (5.1.3) in the case of a solid powder. Titrate with the Karl Fischer reagent using the same electrometric procedure for detecting the end-point of the reaction.

Note the volume (V_4) of Karl Fischer reagent used for the determination.

NOTE — It is advisable to use a test portion such that its water content corresponds to a volume of Karl Fischer reagent that can be measured with sufficient accuracy. If necessary, increase in proportion the quantities of solvent and test sample used and then use a titration vessel of suitable capacity.

7.3 Expression of results

7.3.1 *Water equivalent of the Karl Fischer reagent*

The water equivalent T of the Karl Fischer reagent (4.5), expressed in milligrams of water per millilitre of reagent, is given by the formula

$$T = \frac{m_3 \times 0{,}156\,6}{V_3} \quad \text{or} \quad T = \frac{m_4}{V_3}$$

where

m_3 is the mass, in milligrams, of the sodium tartrate (4.6) introduced if this reagent is used for the standardization (7.2.1);

m_4 is the mass, in milligrams, of water introduced if pure water is used for the standardization;

V_3 is the volume, in millilitres, of the Karl Fischer reagent (4.5) used for the standardization;

0,156 6 is the factor for calculation of the water of the sodium tartrate dihydrate.

7.3.2 *Water content of the sample*

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

$$\frac{V_4 \times T}{m_0 \times 10} \quad \text{or} \quad \frac{V_4 \times T}{V_0 \times \rho \times 10}$$

where

m_0 is the mass, in grams, of the test portion (in the case of solid products);

V_0 is the volume, in millilitres, of the test portion (in the case of liquid products);

ρ is the density of the sample, in grams per millilitre, at 20 °C (in the case of liquid products);

V_4 is the volume, in millilitres, of the Karl Fischer reagent (4.5) used for the determination (7.2.2);

T is the water equivalent, in milligrams per millilitre, of the Karl Fischer reagent, calculated in accordance with 7.3.1.

8 ELECTROMETRIC BACK-TITRATION

8.1 Principle for the detection of the end-point

Addition of an excess of Karl Fischer reagent which is then back-titrated with a standard water/methanol solution. Subjection of the electrodes to a very slight potential difference but sufficient to cause a large deflection of the galvanometer pointer at the start of the back-titration. Indication of the end-point of the titration by the polarization of the cathode accompanied by the sudden interruption of the current (which is shown by a suitable electrical device).

8.2 Procedure

8.2.1 *Standardization of the Karl Fischer reagent*

8.2.1.1 Assemble the apparatus as shown in annex C, lubricating the joints with the grease (4.10). Place in the titration vessel (5.2.1.2) sufficient Karl Fischer reagent (4.5) from one of the automatic burettes (5.2.1.1) to cover the electrodes (5.2.1.4). Switch on the electromagnetic stirrer (5.2.1.5) and close the circuit of the device for the electrometric detection of the end-point (5.2.1.6). Allow the standard water/methanol solution (4.8) to flow from the second automatic burette (5.2.1.1) until the pointer of the galvanometer moves suddenly to zero.

8.2.1.2 In the small glass tube (5.2.3), weigh, to the nearest 0,000 1 g, approximately 0,250 g of the sodium tartrate (4.6). Place this in the titration vessel very quickly, removing the "vaccine cap" for a few seconds, then weigh the small glass tube, so as to determine, by difference, the mass (m_5) of the sodium tartrate used.

Standardization may also be effected by introducing a mass (m_6) of water of approximately 0,040 g from a dropping bottle, weighed before and after introduction into the titration vessel.

Then add a known excess volume (V_5) of the Karl Fischer reagent, stopping when the solution becomes brown in colour. Wait for 30 s and back-titrate this excess, using the standard water/methanol solution (4.8), until the pointer of the galvanometer moves suddenly to zero. Note the volume (V_6) of this solution (4.8) used.

8.2.2 *Correspondence between the Karl Fischer reagent and the standard water/methanol solution*

Partially empty the titration vessel (5.2.1.2), leaving the electrodes submerged in the liquid neutralized as specified in 8.2.1.

Add 20 ml of the Karl Fischer reagent (4.5), measured in the first automatic burette (5.2.1.1), and titrate with the standard water/methanol solution (4.8) contained in the second automatic burette, until the pointer of the galvanometer moves suddenly to zero. Note the volume (V_7) of this solution (4.8) used.

8.2.3 *Determination*

Empty the titration vessel (5.2.1.2) by means of its drain tap. Place in it 25 ml (or the volume specified in the procedure for the product to be analysed) of the methanol (4.1), using a syringe (5.2.2) passing through the "vaccine cap". Switch on the electromagnetic stirrer (5.2.1.5).

In order to cause reaction of the traces of water present in the methanol, add a slight excess (approximately 2 ml) of the Karl Fischer (4.5) and then add the standard water/methanol solution (4.8) until the pointer of the galvanometer moves suddenly to zero.

Introduce the specified test portion by means of a syringe in the case of a liquid or weighed to the nearest 0,000 1 g in a small glass tube (5.2.3) in the case of a solid powder.

Add a known excess volume (V_8) of the Karl Fischer reagent, stopping when the solution becomes brown in colour. Wait for 30 s and back-titrate this excess, using the standard water/methanol solution (4.8) until the pointer of the galvanometer moves suddenly to zero.

Note the volume (V_9) of this solution (4.8) used.

NOTE — It is advisable to use a test portion such that its water content corresponds to a volume of Karl Fischer reagent that can be measured with sufficient accuracy. If necessary, increase in proportion the quantities of methanol and test sample used and then use a titration vessel of suitable capacity.

8.3 Expression of results

8.3.1 *Water equivalent of the Karl Fischer reagent*

The water equivalent T of the Karl Fischer reagent (4.5), expressed in milligrams of water per millilitre of reagent, is given by the formula

$$T = \frac{m_5 \times 0{,}156\,6}{V_5 - \left(V_6 \times \frac{20}{V_7}\right)} \quad \text{or} \quad T = \frac{m_6}{V_5 - \left(V_6 \times \frac{20}{V_7}\right)}$$

where

m_5 is the mass, in milligrams, of the sodium tartrate (4.6) introduced if this reagent is used for the standardization (8.2.1.2);

m_6 is the mass, in milligrams, of water introduced if pure water is used for the standardization (8.2.1.2);

V_5 is the known excess volume, in millilitres, of the Karl Fischer reagent (4.5) added in 8.2.1.2;

V_6 is the volume, in millilitres, of the standard water/methanol solution (4.8) used in 8.2.1.2 for the back-titration;

V_7 is the volume, in millilitres, of the standard water/methanol solution (4.8) used in 8.2.2 (correspondence with the Karl Fischer reagent);

0,156 6 is the factor for calculation of the water of the sodium tartrate dihydrate.

8.3.2 *Water content of the sample*

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

$$\left[V_8 - \left(V_9 \times \frac{20}{V_7}\right)\right] \times \frac{T}{m_0 \times 10}$$

$$\text{or} \quad \left[V_8 - \left(V_9 \times \frac{20}{V_7}\right)\right] \times \frac{T}{V_0 \times \rho \times 10}$$

where

m_0 is the mass, in grams, of the test portion (in the case of solid products);

V_0 is the volume, in millilitres, of the test portion (in the case of liquid products);

ρ is the density of the sample, in grams per millilitre, at 20 °C (in the case of liquid products);

V_7 is as defined in 8.3.1;

V_8 is the known excess volume, in millilitres, of the Karl Fischer reagent (4.5) added in 8.2.3;

V_9 is the volume, in millilitres, of the standard water/methanol solution (4.8) used in 8.2.3 for the back-titration;

T is the water equivalent, in milligrams per millilitre, of the Karl Fischer reagent, calculated in accordance with 8.3.1.

9 TEST REPORT

The test report shall include the following particulars :

a) an identification of the sample;

b) the reference of the method used;

c) the results and the method of expression used;

d) any unusual features noted during the determination;

e) any operation not included in this International Standard or regarded as optional.

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ANNEX A

STANDARDIZATION OF KARL FISCHER REAGENT WITH STANDARD WATER/METHANOL SOLUTION

A.1 VISUAL METHOD

A.1.1 If the standard water/methanol solution (4.7) is used instead of the sodium tartrate (4.6) to standardize the Karl Fischer reagent (4.5), sub-clause 6.2.1.2 relating to visual titration is amended as follows :

Using a syringe (5.1.2), add 10,0 ml of the methanol (4.1) to the titration vessel; titrate with the Karl Fischer reagent (4.5) until the same brown colour as in 6.2.1.1 is obtained, and note the volume (V_{10}) of reagent used.

In the same way, add 10,0 ml of the standard water/methanol solution (4.7). Titrate the known quantity of water thus introduced with the Karl Fischer reagent (4.5) to be standardized, until the same brown colour is obtained, and note the volume (V_{11}) of reagent used.

A.1.2 In addition, sub-clause 6.3.1 is amended as follows :

The water equivalent T of the Karl Fischer reagent (4.5), expressed in milligrams of water per millilitre of reagent, is given by the formula

$$T = \frac{100}{V_{11} - V_{10}}$$

where

100 is the mass, in milligrams, of water contained in 10 ml of the standard water/methanol solution (4.7);

V_{10} is the volume, in millilitres, of the Karl Fischer reagent (4.5) used for the titration of the 10 ml of the methanol (4.1);

V_{11} is the volume, in millilitres, of the Karl Fischer reagent (4.5) used for the titration of the 10 ml of the standard water/methanol solution (4.7).

A.2 ELECTROMETRIC METHOD – DIRECT TITRATION

A.2.1 If the standard water/methanol solution (4.7) is used instead of the sodium tartrate (4.6) to standardize the Karl Fischer reagent (4.5), sub-clause 7.2.1.2 relating to direct electrometric titration is amended as follows :

Using a syringe (5.1.2), add 10,0 ml of the methanol (4.1) to the titration vessel; titrate with the Karl Fischer reagent (4.5) until the same deflection of the pointer of the galvanometer is reached and remains stable for at least 1 min, and note the volume (V_{12}) of reagent used.

In the same way, add 10,0 ml of the standard water/methanol solution (4.7). Titrate the known quantity of water thus introduced with the Karl Fischer reagent (4.5) to be standardized until the same deflection of the pointer of the galvanometer is reached and remains stable for at least 1 min. Note the volume (V_{13}) of reagent used.

A.2.2 In addition, sub-clause 7.3.1 is amended as follows :

The water equivalent T of the Karl Fischer reagent (4.5), expressed in milligrams of water per millilitre of reagent, is given by the formula

$$T = \frac{100}{V_{13} - V_{12}}$$

where

100 is the mass, in milligrams, of water contained in 10 ml of the standard water/methanol solution (4.7);

V_{12} is the volume, in millilitres, of the Karl Fischer reagent (4.5) used for the titration of the 10 ml of the methanol (4.1);

V_{13} is the volume, in millilitres, of the Karl Fischer reagent (4.5) used for the titration of the 10 ml of the standard water/methanol solution (4.7).