International Standard 5381

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Starch hydrolysis products — Determination of water content — Modified Karl Fischer method

Produits d'hydrolyse de l'amidon ou de la fécule — Dosage de l'eau — Méthode Karl Fisher modifiée

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (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 authorized 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.

International Standard ISO 5381 was developed by Technical Committee ISO/TC 93, *Starch (including derivatives and by-products)*, and was circulated to the member bodies in April 1982.

It has been approved by the member bodies of the following countries :

Canada	Germany, F.R.	South Africa, Rep. of
Egypt, Arab Rep. of	Netherlands	USA
France	Poland	USSR

No member body expressed disapproval of the document.

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0 Introduction

This International Standard is based on the method described in ISO 760. However, it has been improved by determining the content directly using the methanol/formamide solvent.

1 Scope and field of application

This International Standard specifies a method for the determination of the water content of starch hydrolysis products.

2 Reference

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

3 Principle

Reaction of a solution of iodine, sulphur dioxide, pyridine and 2-methoxyethanol (stabilized Karl Fischer reagent) with the water contained in the product dispersed previously in a mixture of methanol and formamide.

4 Reactions

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

$$C_5H_5N.SO_3 + ROH \rightarrow C_5H_5NH.OSO_2OR$$

where R is the 2-methoxyethyl radical.

5 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity; all solvents shall have a water content of less than 0,1 % (*m/m*).

5.1 "Stabilized" Karl Fischer reagent.

The stabilized reagent is commercially available in the form of a prepared solution. It is also possible to prepare the reagent in the laboratory (see ISO 760).

5.2 Methanol/formamide solvent.

Mix 700 ml of anhydrous methanol with 300 ml of anhydrous formamide.

This reagent shall be handled with care.

5.3 Sodium tartrate, crystalline ($Na_2C_4H_4O_6 \cdot 2H_2O$).

This product is commercially available in the form "special quality for Karl Fischer". If this quality cannot be obtained, wash the tartrate with 10 ml of the methanol/formamide solvent (5.2), and carry out an appropriate blank test.

Crush the product so that it passes completely through a sieve of nominal aperture size 250 µm, complying with the requirements of ISO 565. The water content of this hydrate is approximately 15,66 % (*m/m*) and shall be checked by vacuum drying at 150 °C until constant mass is obtained.

6 Apparatus

Ordinary laboratory apparatus, in particular

6.1 One-mark pipette, of capacity 20 ml.

6.2 Devices, into which the sample to be analysed can be introduced.

6.2.1 Weighing tube (for solid products), consisting of a test tube of suitable diameter so as to allow the introduction of samples, and fitted with a stopper.

6.2.2 Syringe (for viscous liquids), of capacity 10 ml, for example in accordance with annex A.

6.2.3 One-mark pipettes (for liquid products), of appropriate capacities.

6.3 Karl Fischer titrating equipment or similar apparatus (see the illustrations in annex B).

6.4 Analytical balance.

7 Procedure

7.1 Preparation of the apparatus

The reagents shall be standardized for each daily series of tests and the apparatus set up in conformity with the manufacturer's instructions.

If the apparatus has remained assembled for more than 24 h, it is recommended that the reagent be poured back into the tank and that the burette be filled several times before commencing a series of titrations.

If the titration vessel of the apparatus has not been used before, or after emptying, pour in 20 ml of the methanol/formamide solvent (5.2) either by means of a pipette fitted with a bulb (6.1), or by means of the device fitted in the apparatus used.

This quantity should be adequate for immersing the ends of the platinum electrodes having adjusted the position of these electrodes in such a way as not to obstruct the stirrer during its rotation.

Adjust the rate of stirring and add the Karl Fischer reagent (5.1) until the equivalence point is reached and maintained for a period of 60 s (see 7.3).

Successive samples to be analysed can be added to the liquid remaining in the titration vessel. When the vessel is full, empty it by means of suction using a siphon tube introduced through the circular aperture in the cover or through the valve at the bottom of the vessel.

7.2 Standardization of the Karl Fischer reagent

Weigh, to the nearest 0,5 mg, approximately 500 to 700 mg of the sodium tartrate (5.3) (according to the type of apparatus) in the weighing tube (6.2.1) and introduce it into the titration vessel. Weigh the tube again to determine the exact mass (m_0) of sodium tartrate introduced.

Leave for 3 min to allow the sodium tartrate to dissolve.

Then titrate using the Karl Fischer reagent (5.1) until the equivalence point is reached again, as in 7.1 (see the notes to 7.4.3.3). Note the volume (V_0) of reagent used. Repeat the determination until two successive titrations agree to at least 0,2 % of the mean.

7.3 Correction

The dispersion of the samples and the extraction of the water contained in the samples takes time and the value of the titre can change during this period. This is why it is necessary to make a correction taking into account this change by taking the same time for standardizing the reagent.

7.4 Determination

7.4.1 Preparation of the test sample

7.4.1.1 Liquid or viscous products

Mix the laboratory sample. If necessary, warm slightly to obtain a homogeneous mixture.

7.4.1.2 Solid products

Crush the laboratory sample so that it passes easily through a sieve of nominal aperture size 500 µm, complying with the requirements of ISO 565.

7.4.2 Test portion

7.4.2.1 Liquid or viscous products

Using a pipette (6.2.3) or a special syringue (6.2.2), take a quantity of the test sample (7.4.1.1) so that a volume of approximately 20 ml of the Karl Fischer reagent is necessary when using a 25 ml burette, corresponding to approximately 120 mg of water.

7.4.2.2 Solid products

In the weighing tube (6.2.1), weigh, to the nearest 0,1 mg, a quantity of the test sample (7.4.1.2) so that a volume of approximately 20 ml of the Karl Fischer reagent is necessary when using a 25 ml burette.

7.4.3 Titration

7.4.3.1 Place the test portion (7.4.2) into the titration vessel as quickly as possible and determine the exact mass added in the case of solid products or viscous liquids by reweighing the weighing tube or syringe.

7.4.3.2 Switch on the stirrer and stir until the sample is completely dispersed so as to allow total extraction of the water. Note the time necessary for obtaining good dispersion.

7.4.3.3 Titrate with the Karl Fischer reagent (5.1) as indicated in 7.1 until the equivalence point is reached.

NOTES

1 The Karl Fischer reagent has a very dark colour. It is recommended that the graduations of the burette be read at the top of the column of liquid and not at the bottom of the meniscus.

2 If an automatic apparatus is used, the burette is filled so that the bottom of the meniscus is at the same level as the burette graduation. Therefore, it is necessary to add 0,1 ml to each reading to take this into account.

7.4.4 Number of determinations

Carry out two determinations on the same test sample (7.4.1).

8 Expression of results

8.1 Method of calculation and formulae

8.1.1 Water equivalent of the Karl Fischer reagent

The water equivalent, T, of the Karl Fischer reagent, expressed in milligrams of water per millilitre of reagent, is given by the fomula

$$\frac{m_0 \times H}{100 \times V_0}$$

where

m_0 is the mass, in milligrams, of the sodium tartrate (5.3) used for the standardization (7.2);

H is the water content, expressed as a percentage by mass, of the sodium tartrate used, determined according to 5.3;

V_0 is the volume, in millilitres, of the Karl Fischer reagent used for the standardization (7.2).

8.1.2 Water content of the product

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

$$\frac{V \times T \times 100}{m}$$

where

V is the volume, in millilitres, of the Karl Fischer reagent used for the titration (7.4.3);

m is the mass, in milligrams, of the test portion (7.4.2);[1)]

T is the water equivalent, expressed in milligrams per millilitre, of the Karl Fischer reagent, determined according to 8.1.1.

Take as the result the arithmetic mean of the two determinations provided that the requirement for repeatability (see 8.2) is satisfied.

8.2 Repeatability

The difference between the results of two determinations carried out simultaneously or in rapid succession on the same sample by the same analyst shall not exceed :

- 0,05 for water contents less than 1 % (m/m);
- 0,1 for water contents between 1 and 10 % (m/m);
- 0,15 for water contents between 10 and 20 % (m/m);
- 0,2 for water contents greater than 20 % (m/m).

9 Test report

The test report shall show the method used and the result obtained, clearly indicating the method of expression used. It shall also mention any operating details not specified in this International Standard, or regarded as optional, as well as any circumstances likely to have influenced the results.

The test report shall give all the details required for the complete identification of the sample.

1) For liquid products, this mass is equal to the volume of the sample taken by pipette multiplied by its density.

Annex A

Special syringe for adding samples in the form of viscous liquids and its method of use

A.1 Method of construction (see figure 1)

Take a syringe of nominal capacity 10 ml and cut off the end.

Using a conical-shaped grinding wheel, enlarge the hole at the small end until it is about 8 to 9 mm.

Take a standard 10/24 conical male ground glass joint and glue its large end with epoxy resin.

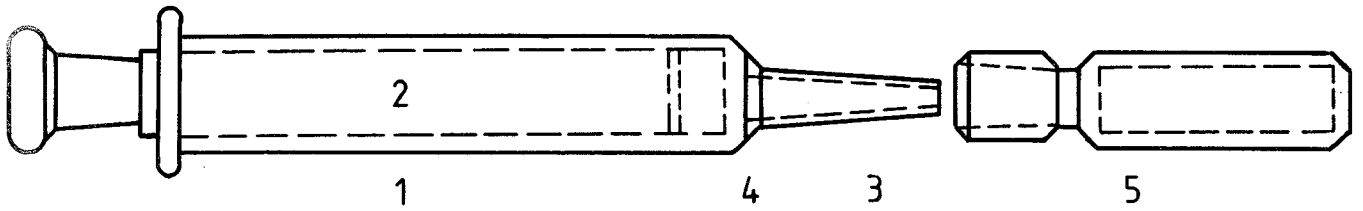
Fit a sleeve comprising a tube with a standard 10/19 conical ground glass joint (female).

A.2 Method of use

Place the sleeve on the modified syringe and immerse the end with the sleeve into the viscous liquid so that the end of the sleeve is just below the surface.

Completely withdraw the piston of the syringe and hold it in that position until the required quantity of the sample has been pumped into the syringe. Release the piston, remove the syringe from the sample and take off the sleeve. Wipe the end of the modified syringe to remove any excess liquid and cover with a small rubber bulb. Weigh the syringe and its contents.

Remove the bulb and insert the end of the syringe in the aperture in the titration vessel of the Karl Fischer apparatus for introducing the sample. Push in the piston to release the contents of the syringe, withdraw the syringe, plug the aperture of the titration vessel, put back the bulb on the end and reweigh the syringe to determine the exact mass of sample introduced into the titration vessel.



1 Body of the syringe

2 Piston

3 Standard conical ground glass joint (male)

4 Epoxy resin neck

5 Added tube with conical ground glass joint (female)

Figure 1 — Special syringe

Annex B

Illustrations of Karl Fischer apparatus (for information only)

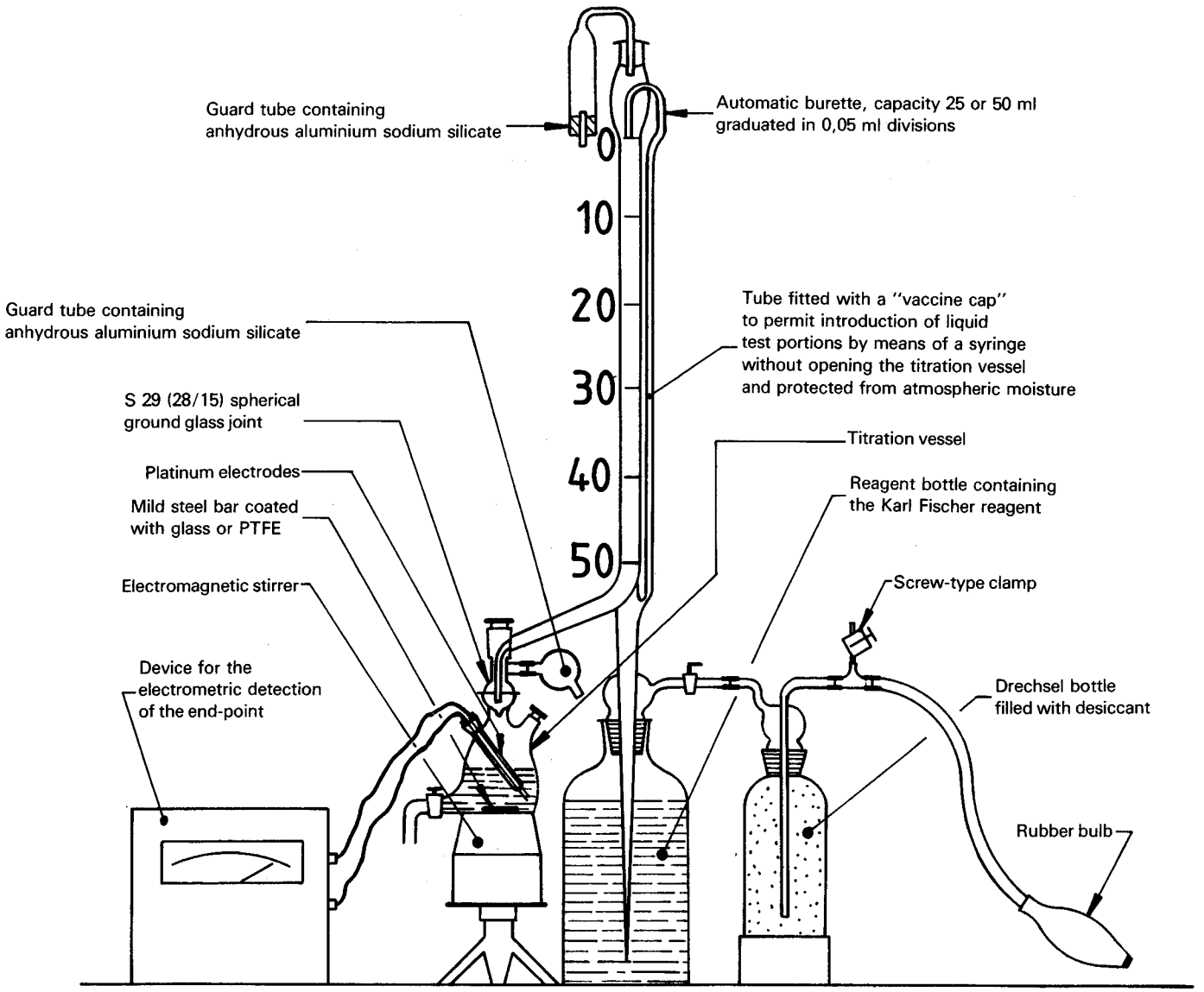


Figure 2 — General arrangement

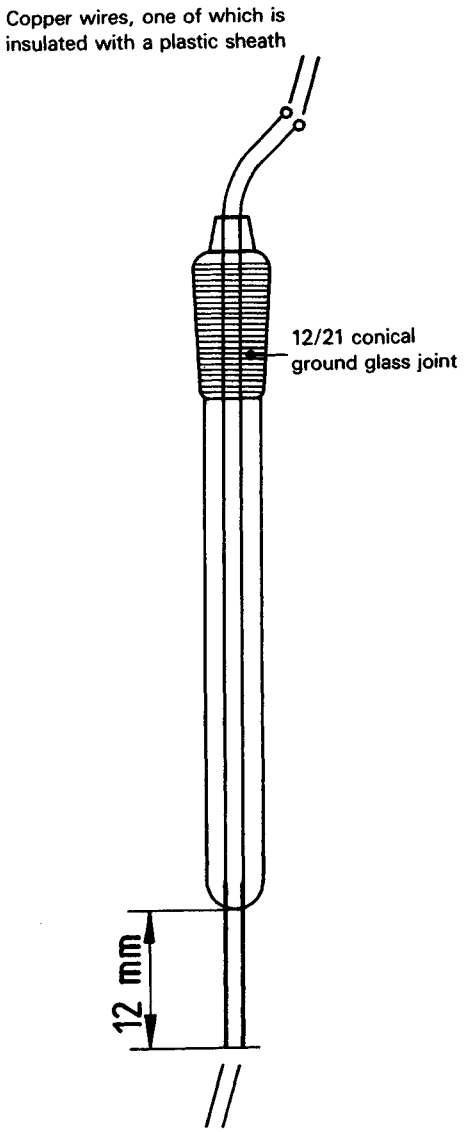


Figure 3 — Platinum electrodes

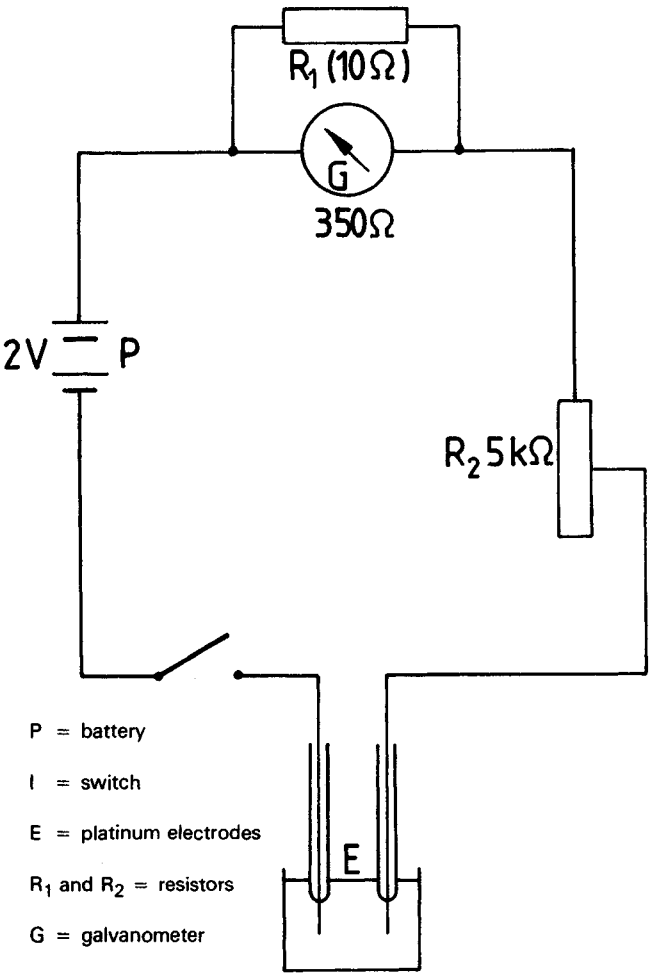


Figure 4 — Circuit for the device for the electrometric detection of the end-point