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Plastics — Determination of water content

Plastiques — Dosage de l'eau

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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 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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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The committee responsible for this document is ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*.

This fourth edition cancels and replaces the third edition (ISO 15512:2014), of which it constitutes a minor revision to update information in 6.2.1.

Introduction

The interlaboratory comparability of the water content determination of plastics is often low. Major causes for this are the sample packaging, sample handling, and differences between equipment and settings. Samples have to, e.g. be packed in special glass containers or water barrier sealed bags. Sample handling is preferably to be carried out in a dry nitrogen or air environment. For improving the repeatability and reproducibility, the procedure prescribed in this International Standard is intended to be followed strictly.

The temperature settings for the vaporization method are not specified in this International Standard. For the manometric method, a temperature of 200 °C is often used. However, for some condensation materials, this might be too high and could, e.g. cause generation of water due to a condensation reaction.

The heating temperature has to be optimized concerning the material to be tested, the equipment in use, and the practical circumstances. If the temperature is too low, the total amount of water in the material to be tested will not be evaporated completely, whereas too high temperatures cause water generation due to effects like degradation and condensation reactions.

In this International Standard, a procedure is included for optimization of the heating temperature in order to choose the correct temperature for the water content determination and to improve the interlaboratory comparability.

Plastics — Determination of water content

1 Scope

1.1 This International Standard specifies methods for the determination of the water content of plastics in the form of powder, granules, and finished articles. These methods do not test for water absorption (kinetics and equilibrium) of plastics as measured by ISO 62.

Method A is suitable for the determination of water content as low as 0,1 % with an accuracy of 0,1 %. Method B and Method C are suitable for the determination of water content as low as 0,01 % with an accuracy of 0,01 %.

Water content is an important parameter for processing materials and has to remain below the level specified in the appropriate material standard.

1.2 Four alternative methods are specified in this International Standard.

— **Method A** is an extraction method using anhydrous methanol followed by a Karl Fischer titration of the extracted water. It can be used for all plastics and is applicable to granules smaller than 4 mm × 4 mm × 3 mm. The method can also be used for, e.g. prepolymer materials in the form of a powder that are insoluble in methanol.

— **Method B1** is a vaporization method using a tube oven. The water contained in the test portion is vaporized and carried to the titration cell by a dry air or nitrogen carrier gas, followed by a Karl Fischer titration of the collected water. It can be used for all plastics and is applicable to granules smaller than 4 mm × 4 mm × 3 mm.

— **Method B2** is a vaporization method using a heated sample vial. The water contained in the test portion is vaporized and carried to the titration cell by a dry air or nitrogen carrier gas, followed by a Karl Fischer titration of the collected water. It can be used for all plastics and is applicable to granules smaller than 4 mm × 4 mm × 3 mm.

— **Method C** is a manometric method. The water content is determined from the increase in pressure, which results when the water is evaporated under a vacuum. This method is not applicable to plastic samples containing volatile compounds, other than water, in amounts contributing significantly to the vapour pressure at room temperature. Checks for the presence of large amounts of volatile compounds are to be carried out periodically, for example by gas chromatography. Such checks are particularly required for new types or grades of material.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

3 Method A — Extraction with anhydrous methanol

3.1 Principle

A test portion is extracted with anhydrous methanol and the extracted water determined by titration using the Karl Fischer method.

3.2 Reagents

During the analysis, use only reagents of recognized analytical grade.

3.2.1 Titration medium, methanol anhydrous, having a water content less than 0,1 % by mass. Other solvents can be used if shown to be comparable.

3.2.2 Karl Fischer reagent, with an equivalence factor of approximately 3 mg/ml to 5 mg/ml of water. When the reagent is prepared, check its equivalence factor as specified in ISO 760.

3.3 Apparatus

Ordinary laboratory apparatus and the following.

3.3.1 Glass flasks, approximately 250 ml capacity, provided with a suitable cap preventing moisture uptake or release.

3.3.2 Conical titration flasks, approximately 150 ml capacity, with standard ground necks and provided with ground-glass stoppers.

3.3.3 Reflux condensers, with ground neck capable of being fitted on to the flasks (3.3.2) and on to the tubes (3.3.4).

3.3.4 Water-absorption tubes with ground joints, containing calcium chloride or other suitable drying agent.

3.3.5 Heaters, suitable for the conical titration flasks (3.3.2).

3.3.6 Desiccator, containing a suitable desiccant.

3.3.7 Analytical balance, accurate to 0,2 mg.

3.3.8 Karl Fischer apparatus, for determining water content in accordance with ISO 760.

3.4 Preparation of test sample

3.4.1 Granules or powder

Take a representative sample of approximately 100 g. Put the sample into a pre-dried glass flask (3.3.1) and immediately close it with a stopper.

NOTE It is desirable to pre-dry the container in an oven and then cool it over a suitable desiccant.

3.4.2 Finished articles

Cut or saw the sample into pieces of appropriate size, i.e. having a maximum size of 4 mm × 4 mm × 3 mm. Proceed quickly to minimize moisture absorption.

3.5 Procedure

3.5.1 Precautions

Due to the low quantities of water measured, maximum care shall be exercised at all times to avoid contaminating the sample with water from the sample container, the atmosphere, or transfer equipment. Hygroscopic resin samples shall be protected from the atmosphere.

3.5.2 Preparation of test portions

Conduct the test on two test portions from the same sample. Use test portions containing 10 mg to 20 mg of water based on the estimated water content of the sample.

Using modern coulometric Karl Fischer titration instruments test portions containing less than 10 mg can be applied if the same level of accuracy of results can be achieved.

3.5.3 Determination

Carefully dry the apparatus.

Weigh each test portion to the nearest 1 mg into a conical titration flask (3.3.2) fitted with a ground-glass stopper. Pipette 50 ml of anhydrous methanol (3.2.1) into the conical flask containing the test portion. At the same time, pipette 50 ml of anhydrous methanol to another conical flask for a blank test. Stopper the flasks. Keep the stoppered flasks in the desiccator (3.3.6) pending continuation of the test.

Unstopper the flasks and quickly attach them to reflux condensers (3.3.3) fitted with calcium chloride tubes (3.3.4). Reflux the contents of the conical flasks for 3 h, then leave them for 45 min to cool to room temperature. Separate the flasks from the condensers, quickly stopper them, and place them in the desiccator.

Use the Karl Fischer apparatus (3.3.8) to titrate the contents of each flask with Karl Fischer reagent (3.2.2).

NOTE Alternative sample preparation methods and titration methods are given in Annex A.

3.6 Expression of results

The water content, w, expressed as a percentage by mass, for each of the two determinations is given by Formula (1):

$$w = \frac{\left(V_1 - V_2\right) \times T}{m} \times 100 \qquad (1)$$

where

V_1 is the volume, expressed in millilitres, of Karl Fischer reagent used for the determination;

V_2 is the volume, expressed in millilitres, of Karl Fischer reagent used for the blank test;

T is the water equivalent, expressed in grams of water per millilitre of reagent, of Karl Fischer reagent;

m is the mass, in grams, of the test portion.

NOTE For some equipment, V_2 might not be available separately but only used for internal calculation of V_1 - V_2. In this case, the numerator in the formula simplifies to $V \times T$.

The two values for the water content shall not differ by more than 10 % relative or 0,02 % absolute, whichever is the greater. If the difference is greater, repeat the measurements until acceptable consecutive values are obtained and discard all unacceptable results.

The result is expressed as the average of these two determinations, rounded to the nearest 0,01 % by mass.

3.7 Precision

The precision of this test method is not known because interlaboratory data are not available. If and when interlaboratory data are obtained, a precision statement will be added to a subsequent revision.

For comparison of data between two laboratories, special care needs to be taken on sample packing and sample handling.

4 Method B1 — Water vaporization using a heating tube oven

4.1 Principle

The sample is weighed then placed in an oven. The water contained in the test portion is vaporized and carried to the titration cell by a dry nitrogen carrier gas. The water is then titrated using the coulometric Karl Fischer method. This method is based on the reduction of iodine by sulfur dioxide in the presence of water to form sulfur trioxide and hydroiodic acid as follows:

$$I_2 + SO_2 + H_2O \rightarrow 2HI + SO_3$$

Unlike the conventional Karl Fischer reagents that include iodine, the coulometric technique generates the iodine electrolytically from iodide:

$$2I^- \rightarrow I_2 + 2e^-$$

with 10,71 C of generating current corresponding to 1 mg of water in accordance with Faraday’s Law.

4.2 Reagents

During the analysis, use only reagents of recognized analytical grade.

4.2.1 Anode solution, containing iodide ions to generate iodine in the reaction mixture, in accordance with the equipment manufacturer’s instructions.

4.2.2 Cathode solution, containing a suitable salt in methanol (or another suitable organic solvent), prepared in accordance with the equipment manufacturer’s instructions.

4.2.3 Universal single anode reagent, containing iodide ions to generate iodine in the reaction mixture, in accordance with the equipment manufacturer’s instructions, for use in a diaphragm-free cell.

NOTE A universal single anode coulometric reagent is applied in diaphragm-free titration cells. Titration cells with diaphragm require the use of a separate anode and cathode solution.

4.2.4 Neutralization solution, consisting of approximately 4 mg/ml of water in propylene carbonate, ethylene glycol monomethyl ether (2-methoxyethanol), or methyl cellosolve.

4.2.5 Nitrogen gas (N_2), containing less than 5 µg/g of water.

4.3 Apparatus

Ordinary laboratory apparatus and the following.

4.3.1 Coulometric Karl Fischer titrator, consisting of a control unit and a titration-cell assembly equipped with a generator cell, with or without diaphragm, dual platinum sensing electrodes, and a magnetic stirrer (see Figure 1).

The instrument is designed to coulometrically generate iodine that reacts stoichiometrically with the water present in the cell. The coulombs of electricity required to generate the reagent are converted to micrograms of water and is given as a direct digital readout.

NOTE A diaphragm-free cell is accurate enough for many applications. However, some applications may require a diaphragm for the best possible accuracy. This can be checked with the equipment supplier.

4.3.2 Water vaporizer, consisting of an oven capable of heating the sample to at least 300 °C, a heating tube (see Figure 2), a temperature control unit, a carrier-gas flow meter, and carrier-gas drying tubes containing desiccant.

4.3.3 Microsyringe, with capacity of 10 µl, calibrated.

4.3.4 Sample boat.

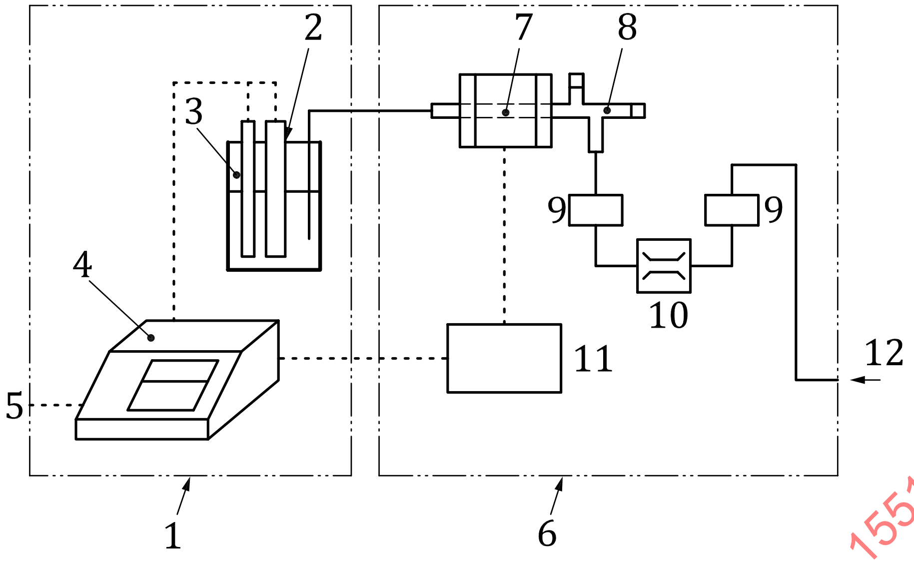
Aluminium foil can be used to hand-fashion a disposable boat large enough to contain the sample and small enough to fit into the heating tube.

4.3.5 Suitable desiccant, for the carrier-gas drying tubes (4.3.2).

4.3.6 Molecular sieve, pore size 0,3 nm, desiccant for carrier gas.

4.3.7 PTFE sleeves, to be used to maintain the air-tightness of the ground glass joints of the system.

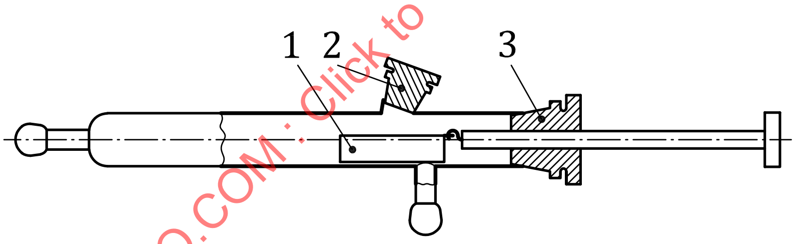
Alternatively, grease, containing little or no water and having low water absorptivity, can be used.



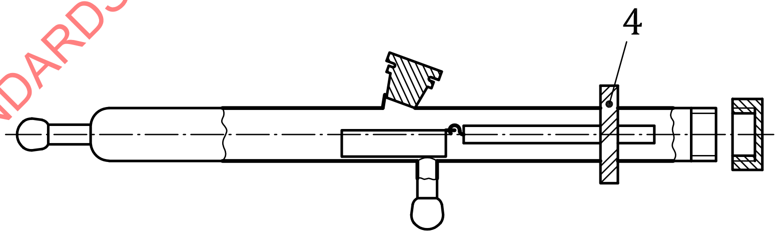
Key

1	coulometric Karl Fischer meter	7	oven
2	exhaust gas	8	heating tube
3	titration cell	9	water-absorption tubes (filled with desiccant, for example P_2O_5)
4	titration controller	10	flow meter
5	power supply	11	temperature controller
6	water vaporizer	12	N_2 gas

Figure 1 — Flowchart of a system used for the determination of water content using method B1



a) Push-bar type



b) Magnet type

Key

1	sample boat	3	sample-boat inlet
2	sample inlet	4	magnet

Figure 2 — Heating tubes

4.4 Preparation of test sample

The test material can be in any form, such as granules, moulding powder, fabricated shapes, or moulded items.

Cut fabricated shapes and moulded items to a suitable size. Granules shall be smaller than 4 mm × 4 mm × 3 mm.

Take a representative sample of ≤ 10 g. Due to the small size of the sample, care shall be taken to ensure that it is in fact representative.

4.5 Procedure

4.5.1 Precautions

Due to the low quantities of water measured, maximum care shall be exercised at all times to avoid contaminating the sample with water from the sample container, the atmosphere, or transfer equipment. Hygroscopic resin samples shall be protected from the atmosphere.

4.5.2 Preparation of apparatus

Refer to Figure 1 for the following procedure.

Assemble the water vaporizer (4.3.2) and coulometric Karl Fischer titrator (4.3.1) as directed in the manufacturer's instructions. Fill the absorption tubes with desiccating agent (4.3.2) as directed in the manufacturer's instructions.

Pour approximately 200 ml (adjust for the container size) of the anode solution (4.2.1) into the generator cell and 10 ml of the cathode solution (4.2.2) into the cathode solution cell (4.3.1). The surface of the cathode solution shall be below the level of the anode solution to prevent backflow contamination of the cathode solution.

NOTE A universal single anode coulometric reagent is applied in diaphragm-free titration cells. Titration cells with diaphragm require the use of a separate anode and cathode solution.

Turn the cell power switch on. If the cell potential shows a negative value, indicating that the anode solution contains an excess of iodine, add 50 µl to 200 µl of the neutralization solution (4.2.4).

Disconnect the tube connecting the vaporizer unit to the titration cell. Set the carrier gas flow to 200 ml/min to 300 ml/min and heat the oven to the desired temperature to remove any residual water from the vaporizer (4.3.2).

Lift the titration cell and agitate the solution by gently swirling the cell to remove any residual water from the walls. Stir the solution for a minute in the "TITRATION" mode to dry and stabilize the inner atmosphere.

Reconnect the tube from the vaporizer unit to the titration cell. Keep the carrier-gas flow on during the whole titration. The instrument is then ready for sample analysis.

4.5.3 Equipment check

To check if the coulometric Karl Fischer titrator is functioning properly, carry out a determination with a known amount of water as follows. With the analyser stabilized and in the "READY" position, press the start switch and carefully inject 5 µl of distilled water into the cell using a 10 µl syringe (4.3.3). When the "END" light comes on, record the reading. This reading should be (5 000 ± 250) µg.

To check if the whole system is functioning properly, carry out a determination with 50 mg of sodium tartrate dihydrate ($Na_2C_4H_4O_6 \cdot 2H_2O$) at 150 °C. Follow 4.5.4 to measure the quantity of water contained in the sodium tartrate dihydrate. The result should be (15,6 ± 0,5) %.

4.5.4 Determination

Heat the oven to the desired temperature and place the sample boat (4.3.4) in the heating tube and push it into the oven to dry and also to back purge any residual water contained in the sample-boat inlet.

For the heating temperature, refer to the material standard. As the heating temperature is also dependent on equipment used and the practical circumstances, the heating temperature has to be optimized using the method described in Annex B. If the heating temperature is not mentioned in the material standard or if there is no material standard, then use the method mentioned in Annex B to determine the optimum heating temperature.

After a few minutes, move the sample boat to the sample inlet port and allow it to cool.

Weigh a test portion of the sample (4.4) directly into the sample boat (which will have to be removed from the heating tube for this purpose) or on to a piece of aluminium foil (see next paragraph). Appropriate sizes of test portion are given in Table 1.

If the sample boat is made of glass or another material which is not designed to be discarded after use, a piece of aluminium foil can be wrapped around the test portion to prevent the test portion from sticking to the boat when it melts. Wrapping the test portion in this way will also prevent it from scattering during introduction into the sample boat.

If the test portion was weighed directly into the sample boat, place the sample boat back into the heating tube as quickly as possible. If the test portion was weighed on to a piece of aluminium foil, wrap it, and introduce it, again as quickly as possible, into the sample boat either through the sample inlet or the sample-boat inlet.

Table 1 — Recommended mass of test portion

Expected water content w % by mass	**Mass of test portion** m g
$w > 1$	$0{,}2 > m \geq 0{,}1$
$1 \geq w > 0{,}5$	$0{,}4 > m \geq 0{,}2$
$0{,}5 \geq w > 0{,}1$	$1 > m \geq 0{,}4$
$0{,}1 \geq w$	$m \geq 1$

Verify that the instrument is in the “READY” status. Press the “START” key. Move the sample boat into the oven (see Figure 2). Allow the titration to proceed until the “END” light comes on and then record the instrument reading in micrograms.

4.6 Expression of results

Calculate the water content, w, in the test portion, expressed as a percentage by mass by using Formula (2):

$$w = \frac{m_{\text{water}}}{m_{\text{test portion}}} \times 10^{-4} \qquad (2)$$

where

m_{water} is the mass of water found in the test portion, in micrograms;

$m_{\text{test portion}}$ is the mass of the test portion, in grams.

4.7 Precision

The precision of this test method is not known because interlaboratory data are not available. If and when interlaboratory data are obtained, a precision statement will be added to a subsequent revision.

For comparison of data between two laboratories, special care needs to be taken on sample packing and sample handling.

5 Method B2 — Water vaporization using a heated sample vial

5.1 Principle

The sample is weighed into a sample vial and placed in an oven. The water contained in the test portion is vaporized and carried to the titration cell by a dry nitrogen carrier gas. The water is then titrated using the coulometric Karl Fischer method. This method is based on the reduction of iodine by sulfur dioxide in the presence of water to form sulfur trioxide and hydroiodic acid as follows:

$$I_2 + SO_2 + H_2O \rightarrow 2HI + SO_3$$

Unlike the conventional Karl Fischer reagents that include iodine, the coulometric technique generates the iodine electrolytically from iodide:

$$2I^- \rightarrow I_2 + 2e^-$$

with 10,71 C of generating current corresponding to 1 mg of water in accordance with Faraday's Law.

5.2 Reagents

Only reagents of recognized analytical grade shall be used.

5.2.1 Anode solution, containing iodide ions to generate iodine in the reaction mixture, in accordance with the equipment manufacturer's instructions.

5.2.2 Cathode solution, containing a suitable salt in methanol (or another suitable organic solvent), prepared in accordance with the equipment manufacturer's instructions.

5.2.3 Universal single anode reagent, containing iodide ions to generate iodine in the reaction mixture, in accordance with the equipment manufacturer's instructions, for use in a diaphragm-free cell.

NOTE A universal single anode coulometric reagent is applied in diaphragm-free titration cells. Titration cells with diaphragm require the use of a separate anode and cathode solution.

5.2.4 Titration medium, methanol, anhydrous, having a water content < 0,1 % by mass. Other solvents can be used if shown to be comparable.

5.2.5 Water standard 1 %, inorganic substance, water content 1 % (m/m), every lot individually certified.

NOTE The water content can be verified with the method given in Annex C.

5.2.6 Nitrogen gas (N_2), flow of ≥ 60 cm^3/min and preferably containing less than 1 mg/m^3 of water (dew point −80 °C).

NOTE 1 A nitrogen flow of 60 cm^3/min with a water concentration of 1 mg/m^3 corresponds with a water contribution to the titration cell of 0,06 µg H_2O/min.

NOTE 2 For some equipment, a nitrogen flow of ≤ 60 cm^3/min can cause a failure.

5.3 Apparatus

Ordinary laboratory apparatus and the following.

5.3.1 Coulometric Karl Fischer titrator, consisting of a control unit and a titration-cell assembly equipped with a diaphragm-free generator electrode, dual platinum sensing electrodes, and a magnetic stirrer.

The instrument is designed to coulometrically generate iodine, which reacts stoichiometrically with the water present in the cell. The number of coulombs of electricity required to generate the reagent are converted to micrograms of water, presented as a direct digital readout. Adjust the instrument to a start criterion of < 20 µg H_2O/min and a stop criterion of < 5 µg H_2O/min. Adjust the integration time for both criteria to 60 s.

The coulometric Karl Fischer titrator is schematically shown in Figure 3.

NOTE 1 A diaphragm-free cell is accurate enough for many applications. A cell with a diaphragm may be required for the best possible accuracy.

NOTE 2 The start criterion of < 20 µg H_2O/min and the stop criterion of < 5 µg H_2O/min are default values and applicable for most plastics. In case of analysing low concentrations of water, these values might need to be reduced.

NOTE 3 An integration time of 60 s showed to be a suitable starting point for both start and stop criterion.

5.3.2 PTFE sleeves, to be used to maintain the air-tightness of the ground glass joints of the system.

Alternatively, grease, containing little or no water and having low water absorptivity, can be used.

5.3.3 Molecular sieve, pore size 0,3 nm, desiccant for carrier gas.

5.3.4 Water vaporizer, consisting of an oven or a heating device capable of heating a test portion in a sample vial (5.3.5) to at least 300 °C, a temperature control unit, carrier gas, drying tubes containing a molecular sieve, and a carrier gas flow meter.

5.3.5 Sample vials, glass, to be used in the water vaporizer.

The sample vials are dried in a drying oven and kept dry in a desiccator. Sample vials with a capacity of 6 ml are recommended.

5.3.6 Aluminium crimp caps, equipped with a silicone septum, to be used with sample vials.

The crimp caps are dried in a drying oven and kept in a desiccator. Other suitable caps can also be used.

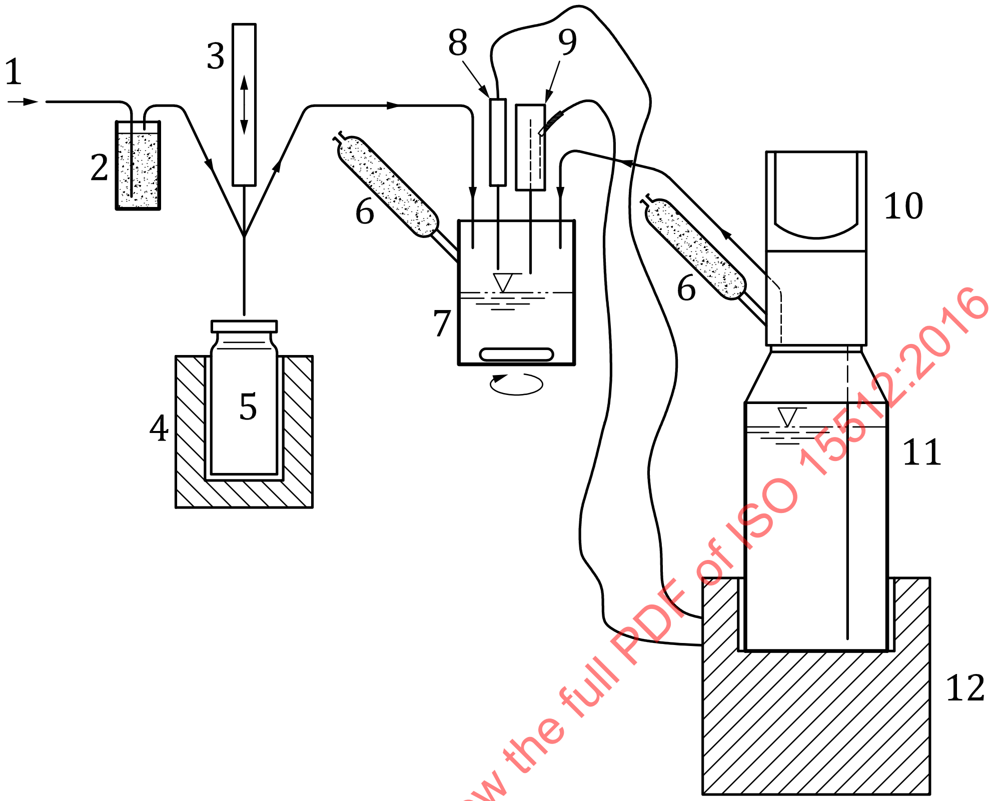
5.3.7 Analytical balance, accurate to 0,1 mg.

5.3.8 Drying oven, temperature 105 °C.

5.3.9 Desiccator, containing an efficient desiccant.

5.3.10 Glass flasks, approximately 250 ml capacity, provided with a suitable cap preventing moisture uptake and release.

5.3.11 Aluminium foil seal bags, approximately 250 g capacity, or other suitable storage container preventing moisture uptake and release.



Key

1	nitrogen supply	7	titration vessel
2	molecular sieve	8	dual platinum electrode
3	oven sample processor	9	generator electrode
4	water vaporizer oven	10	piston burette
5	sample vial	11	universal reagent
6	absorber tube	12	coulometric Karl Fischer titrator

Figure 3 — System setup for the determination of water according to method B2 — Schematic

5.4 Preparation of test sample

The absolute amount of water to be determined is in most cases very low. Therefore, maximum care shall be taken to avoid contaminating the sample with water from the sample container, the atmosphere, sample transfer, and/or equipment.

Dry the glass flasks (5.3.10) and the aluminium foil seal bags (5.3.11) at a temperature of 105 °C in a drying oven (5.3.8) for 1 h. Cool and store in a desiccator (5.3.9).

Take a representative test sample of ≥ 100 g, bring this in a dry glass flask or a dry aluminium seal bag and immediately close the glass flask or seal the bag. Store the sample in a desiccator.

The test sample can be in any form, such as granules, moulding powder, fabricated shapes, or moulded items. Granules shall be approximately 4 mm × 4 mm × 3 mm. Other samples shall be cut to approximately the same size as granules.

5.5 Procedure

5.5.1 Preparation of apparatus

Prepare the instrument in accordance with the equipment instructions.

Transfer 100 ml to 150 ml of universal single anode reagent (5.2.3) into the titration vessel and immediately close the vessel.

Set the water vaporizer (5.3.4) to the desired heating temperature (see Annex B) for the material to be analysed. Wait until the temperature is stabilized.

For the heating temperature, refer to the material standard. As the heating temperature is also dependent on equipment used and the practical circumstances, the heating temperature has to be optimized using the method described in Annex B. If the heating temperature is not mentioned in the material standard or if there is no material standard, then use the method mentioned in Annex B to determine the optimum heating temperature.

Take a dry sample vial (5.3.5) and immediately close it with an aluminium crimp cap (5.3.6). Place the sample vial in the water vaporizer and start the titration.

Allow the titration to proceed until the release of water is < 20 µg H_2O/min. The instrument is now prepared for carrying out water determinations.

It is recommended to rinse the transfer line between the water vaporizer and the titration cell assembly with methanol after a series of determinations, as some volatile sample material might deposit in the transfer line.

The universal reagent has a limited capacity with respect to water, which is linearly related to the initial iodine content. Consequently, the reagent needs to be replaced regularly. The capacity of 100 ml universal reagent is equal to 1 000 mg of water. It is advisable to exchange the universal reagent when approximately 80 % of its capacity has been used. Modern instruments can keep record of the total quantity of water absorbed.

5.5.2 Equipment check

Carry out a water determination in order to check if the equipment is functioning properly by analysing 80 mg to 350 mg of the water standard (5.2.5), using the temperature as given in the certificate of the supplier (150 °C to 200 °C). The result shall be within the certified value ± 0,03 % H_2O.

5.5.3 Determination

5.5.3.1 Sample

Select the mass of test portion according the expected moisture content (see Table 2). The sample mass with its absolute mass of water has to be comparable to the absolute mass of water of the water standard.

Carry out a preliminary determination if the water content of the sample is unknown, using 1 g of sample.

As a consequence of the relative small sample amount, special attention should be taken regarding the representativeness of the sample.

In case that the composition of the test sample is unknown, determine the optimum heating temperature (see Annex B).

Table 2 — Recommended mass portion

Expected water content w % by mass	**Mass of test portion** m g
$w > 1$	$0{,}2 > m \geq 0{,}1$
$1 \geq w > 0{,}5$	$0{,}4 > m \geq 0{,}2$
$0{,}5 \geq w > 0{,}1$	$1 > m \geq 0{,}4$
$0{,}1 \geq w$	$5 > m \geq 1$

Place a sample vial (5.3.5) on an analytical balance (5.3.7). Add the selected test portion (see Table 2) into the sample vial and determine the mass of the test portion ($m_{\text{test portion}}$). Immediately close the sample vial with the aluminium crimp cap (5.3.6).

Perform the weighing procedure as quickly as possible to avoid moisture release or pick-up. Carry out the subsequent water determination within 24 h after weighing.

Set the water vaporizer (5.3.4) to the optimum heating temperature for the material to be analysed. Wait until the temperature is stabilized.

Place a closed and empty sample vial in the water vaporizer and record the release of water. Wait until the water release per minute has minimized and is stable below 20 µg H_2O/min (start drift sample Sd_S, see Note). Repeat this step for every water determination.

Place the sample vial in the water vaporizer and start the titration. Lead the nitrogen (5.2.6) with the evaporated water through the solution in the titration cell. The released water, absorbed in the solution, reacts with the electrolytically generated iodine. Allow the titration to proceed until the release of water is < Sd_S + stop criterion (see Note). Record the instrument reading (m_S) in micrograms H_2O and the time the determination has taken (t_S).

NOTE In spite of all precautions and care to avoid water contamination of the used equipment, the instrument continuously generates a small quantity of iodine to react with water, originating from the nitrogen gas, leakage etc. Modern instruments automatically correct for this type of drift.

EXAMPLE 1 If the start criterion is set to < 20 µg H_2O/min and the start drift corresponds to, e.g. 17 µg H_2O/min, the instrument is ready to start. The stop criterion is set to, e.g. < 5 µg H_2O/min. This means that the determination of a subsequent sample is stopped when the iodine generation is below the value (start drift + stop criterion). In this example, the determination is ended if the iodine generation value is below 17+5 = 23 µg H_2O/min. If for example the water determination has taken 6 min, the determined quantity of water has to be subtracted by 6 × 17 = 102 µg H_2O. This correction procedure applies to both sample and blank.

A start criterion of < 20 µg H_2O/min and a stop criterion of < 5 µg H_2O/min are default values and applicable for most water determinations in polymers. Both criteria can be set individually. This becomes inevitable when analysing low water concentrations.

EXAMPLE 2 2 g of a polymer, containing 0,03 % (m/m) water, is analysed and the actual start drift of that determination is 17 µg H_2O/min. If the determination takes 12 min, the determined absolute water quantity has to be corrected for 204 µg H_2O. The sample contains 600 µg H_2O. In general, the correction value should be a fraction of the water quantity in the sample. As a general rule, the correction value should not exceed 10 % of the water content in the sample determined per minute. In this example, the start criterion should be adjusted to, e.g. 0,1 × 600 µg H_2O/12 min = < 5 µg H_2O/min.

5.5.3.2 Blank

Carry out three to five blank determinations, executing the complete determination in the absence of a test sample.

Place a closed and empty sample vial in the water vaporizer and record the release of water. Wait until the water release per minute has minimized and is stabilized below 20 µg H_2O/min (start drift blank Sd_{bl}). Repeat this step for every blank determination.

Place the blank vial in the water vaporizer and start the titration. Lead the nitrogen (5.2.6) with the evaporated water through the solution in the coulometric cell. The released water is absorbed in the solution and reacts with the electrolytically generated iodine. Allow the titration to proceed until the release of water is < (Sd_{bl} + stop criterion). Record the instrument reading (m_{bl}) in micrograms H_2O and the time the determination has taken (t_{bl}).

Use the mean (m'_{bl}) of the individual determinations as blank value in the calculation.

NOTE The blank value results from the water content of the air enclosed in the sample vial, originating from the surrounding air in the laboratory. In a (23 ± 2) °C and (50 ± 10) % relative humidity standard atmosphere, blank values are typically 80 µg H_2O to 100 µg H_2O. Replicate determinations are expected to have a maximum variation of ± 5 µg H_2O from the average.

As the blank value results from the water content of the air enclosed in the sample vial, the blank value varies as a function of the filling height and amount of material in the sample vial. The more material is filled in the vial, the less surrounding air is enclosed and the blank values decrease accordingly. Whether the filling height is negligible or not depends on the absolute blank value and the water content of the sample.

5.6 Expression of results

Calculate the mean value of the blank (m'_{bl}) using Formula (3).

$$m'_{bl} = \frac{\sum \left\{ m_{bl} - \left(t_{bl} \times Sd_{bl} \right) \right\}}{n} \tag{3}$$

where

m_{bl} is the mass of water released during the blank determination, in µg H_2O;

t_{bl} is the time the blank determination has taken, in min;

Sd_{bl} is the start drift blank, in µg H_2O/min;

n is the number of blank determinations.

Calculate the water content of the test sample expressed in % H_2O using Formula (4).

$$w = \frac{m_s - \left(t_s \times Sd_s \right) - m'_{bl}}{m_{\text{test portion}}} \times 10^{-4} \tag{4}$$

where

m_s is the mass of water released from the test portion, in µg H_2O;

t_s is the time the sample determination has taken, in min;

Sd_s is the start drift sample, in µg H_2O/min;

m'_{bl} is the mean of the blank determinations, in µg H_2O

$m_{\text{test portion}}$ is the mass of the test portion, in g.

5.7 Precision

The precision of this test method is not known as interlaboratory data are not available. Interlaboratory data are being obtained and will be added to the subsequent revision.

For comparison of data between two laboratories, special care needs to be taken on sample packing and sample handling.

6 Method C — Manometric method

6.1 Principle

A test portion is heated to a specified temperature in a closed container under vacuum. The water contained in the test sample is vaporized. The resulting pressure increase, which is proportional to the water content, is measured. The water content in the sample is calculated using a calibration factor. The calibration factor is obtained by determining the water loss from a reference material with known water content.

NOTE Every component which, under the conditions of the determination, contributes to the total vapour pressure, gives rise to an equivalent overestimation of the water content.

6.2 Reagents

6.2.1 Water standard, solid material used as standard for the determination of the calibration factor.

The following materials are recommended:

- sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2\ H_2O$), analytical grade, theoretical water content 14,9 % (m/m). The actual water content shall be determined according to Annex C.
- water standard 1 % inorganic substance, water content 1 % (m/m), every lot individually certified.

NOTE If necessary, the water content can be verified with the method given in Annex C.

6.3 Apparatus

Ordinary laboratory equipment and the following.

6.3.1 Manometric moisture analyser.

(Semi-)automatic determination of the water content is preferred. The instrument consists of an electric oven with adjustable temperatures between room temperature and 210 °C, a continuous operating vacuum pump, a glass bulb with of volume of ± 0,5 l, a pressure cell/transmitter, and three switching valves. For the water content determination of powdered materials, the instrument shall be equipped with a flow-restriction add-on.

The manometric moisture analyser is schematically shown in Figure 4.

Set the instrument to a stop criterion (ΔP) of < 8 Pa/5 min.

NOTE 1 The use of an instrument of another design is permitted if comparable results can be obtained.

NOTE 2 The stop criterion, (ΔP) < 8 Pa/5 min, is a default value, applicable for many plastic materials, but can be adjusted when necessary.

6.3.2 Sample tube, borosilicate glass, designed to be used with the manometric moisture analyser, dried during 1 h at a temperature of 105 °C and kept dry in a desiccator.

6.3.3 Drying oven, temperature 105 °C.

6.3.4 Desiccator, containing an efficient desiccant.

6.3.5 Glass flasks, approximately 250 ml capacity, provided with a screw cap preventing moisture uptake and release.

6.3.6 Aluminium foil seal bags, approximately 250 g capacity.

6.3.7 Analytical balance, accurate to 0,1 mg.

6.3.8 Glass beads, diameter approximately 5 mm, dried in a drying oven at 105 °C and kept dry in a desiccator.

6.3.9 Aluminium foil.

6.4 Preparation of test sample

The absolute amount of water to be determined is in most cases very low. Therefore, maximum care shall be taken to avoid contaminating the sample with water from the sample container, the atmosphere, sample transfer, and/or equipment.

Dry glass flasks (6.3.5) and aluminium foil seal bags (6.3.6) in a drying oven (6.3.3). Cool and store in a desiccator (6.3.4).

Take a representative test sample of ≥ 100 g, bring this in a dry glass flask or a dry aluminium foil seal bag, and immediately close the glass flask or seal the bag. Store the sample in a desiccator.

6.5 Procedure

6.5.1 Equipment

6.5.1.1 General

Many modern instruments operate fully automatically or half-automatically. For (half-) automatically operating instruments, the step-by-step instructions described in 6.5.1.2, 6.5.2, and 6.5.3 are not relevant. However, the instrument settings and requirements mentioned in these subclauses, as e.g. the airtight requirement in 6.5.1.2, are mandatory.

For manually operated instruments or further detailed information regarding the procedure, see the relevant step-by-step instructions described in 6.5.1.2 to 6.5.4.

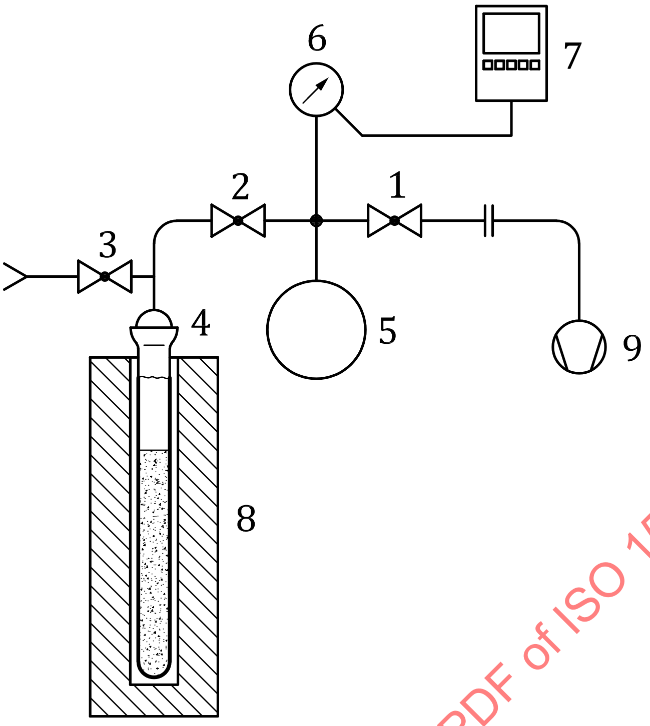
6.5.1.2 Equipment check

The air-tightness of the system can be checked by the following procedure.

- Make sure that valves V-1, V-2, and V-3 are closed.
- Attach a sample tube (6.3.2) to the instrument. Open valves V-1 and V-2. Continue pumping until the absolute pressure value on the display indicates a pressure of < 100 Pa. Close valve V-1. Monitor the pressure increase during a period of 60 min.
- The system is considered to be airtight when the pressure increase after 60 min is < 20 Pa.

In case the system is not airtight, the pressure increase is far more than 20 Pa/h. A pressure increase of slightly more than 20 Pa/h indicates that the system should be outgassed (see 6.5.2).

NOTE It is not necessary to heat the sample tube in the oven in order to check the airtightness of the system.



Key

1	valve V-1	6	pressure gauge
2	valve V-2	7	controller, temperature stability < ± 1 °C
3	valve V-3	8	oven
4	sample tube	9	vacuum pump
5	buffer reservoir, volume 0,5 l		

Figure 4 — System setup for the determination of water content using method C — Schematic

6.5.2 Outgassing

It is necessary to outgas the instrument if used for the first time, after repair, and when volatile components remain in the vacuum system. A constant vacuum is applied to the system in order to evaporate all volatile components. This is carried out by means of the following procedure.

— Make sure that valves V-1, V-2, and V-3 are closed.

— Attach a sample tube (6.3.2) to the instrument and start the vacuum pump. Open valves V-1 and V-2. Continue pumping until the pressure value on the display indicates a pressure of < 100 Pa. Close valve V-1 and V-2 and gradually open valve V-3.

— Air will be introduced into the sample tube until atmospheric pressure. The sample tube can now be removed from the system. Close valve V-3.

NOTE A typical outgas time for a new instrument is 48 h. Typical outgas times after repair or maintenance are 16 h to 24 h.

6.5.3 Calibration

6.5.3.1 Equipment setup

Set the oven to a temperature of 190 °C. Wait until the temperature is stabilized.

Make sure that valves V-1, V-2, and V-3 are closed.

6.5.3.2 Water standard preparation — Sodium molybdate dihydrate

Fold a piece of aluminium foil (6.3.9) into a small cylinder of approximately 3 cm height and 1 cm diameter of which the bottom side is closed. Use e.g. a pen or a pencil to shape the cylinder. Dry the aluminium cylinder during 1 h at 105 °C in a drying oven. Cool the cylinder in a desiccator (6.3.4).

Bring into the aluminium cylinder a quantity of 75 mg to 125 mg sodium molybdate dihydrate (6.2.1) and determine its mass to the nearest 0,1 mg. Close the top of the cylinder slightly by folding the aluminium, bring the cylinder into a sample tube (6.3.2), and immediately attach the tube to the instrument.

Determine the calibration factor following the procedure in 6.5.3.4.

6.5.3.3 Water standard preparation — Inorganic substance

Weigh, to the nearest 0,1 mg, 500 mg to 1 000 mg water standard (6.2.1) in a dry sample tube (6.3.2), cover the material with 2 cm to 3 cm of dry glass beads (6.3.8), and immediately attach the tube to the instrument.

Determine the calibration factor following the procedure in 6.5.3.4.

6.5.3.4 Calibration factor

The instrument calibration factor, *f*, is defined as the mass of water, expressed in milligrams, that causes a pressure difference of 1 Pa. The calibration factor is determined by the following procedure.

Open valve V-1 and then V-2. Wait until the pressure indicates a value < 100 Pa. Close valve V-1. Wait for the pressure to stabilize (typically 15 s to 30 s) and then record the blank pressure, P_0, on the pressure indicator.

Raise the oven until the sample tube is completely inserted into the oven.

The water content determination is ended when the pressure increase in time becomes < 8 Pa/5 min (stop criterion), typically after 15 min to 20 min. Record the pressure, *P*, on the pressure indicator.

Close valve V-2 and open valve V-1 to remove the vaporized water and wait until the pressure is < 100 Pa. Close valve V-1 and V-2 and gradually open valve V-3. Air is introduced into the sample tube until atmospheric pressure. Lower the oven. The sample tube can now be removed from the system. Close valve V-3.

Calculate the instrument calibration factor, *f*, expressed in mg H_2O/Pa, using Formula (5).

$$f = \frac{a \times 0{,}01 \times c}{P - P_0} \qquad (5)$$

where

f is the instrument calibration factor, in mg H_2O/Pa;

a is the mass of water standard used for the calibration, in milligrams;

c is the water content of the water standard as specified by the supplier or determined according to Annex C, in mass %;

P is the pressure after all water has been vaporized, in pascals;

P_0 is the pressure at the start of the determination, in pascals.

Determine the calibration factor by calculating the average of 10 measurements. If a calibration factor deviates more than 3 % relative from the average, the value will be disregarded. If more than three measurements are rejected, the calibration procedure shall be repeated. If still more than three determinations are rejected, the manufacturer shall be contacted.

To prevent powdered material to enter the equipment as a result of the sudden vacuum applied to the sample tube, powdered materials should be put in a small cylinder of dry aluminium foil or covered with dry glass beads in the sample tube. For adding powdered material into the sample tube, a glass powder funnel with the following dimensions is recommended: funnel upper diameter 45 mm, stem length 60 mm, stem outer diameter 13 mm.

NOTE 1 For an instrument with an internal volume of ± 0,5 l, a typical value for the calibration factor, *f*, is approximately 0,005 5 mg H_2O/Pa. As long as the internal volume is not changed, the calibration factor will also not change.

NOTE 2 The end point of the determination is indicated by the pressure increase in time, e.g. < 8 Pa/5 min (stop criterion ΔP). A maximum vaporization time is used to stop the determination when the stop criterion cannot be met within a specified time.

6.5.4 Determination

Select the mass of test portion according to the expected moisture content (see Table 3).

As a consequence of the relative small sample amount, special attention should be taken regarding the representativeness of the sample.

In case that the composition of the test sample is unknown, determine the optimum heating temperature (see Annex B).

Carry out a preliminary determination if the water content of the sample is unknown, using 1 g of sample.

Table 3 — Mass of test portion

Expected water content % m/m	Mass of test portion g
< 0,075	16 ± 1
0,075 to 0,15	10 ± 1
0,15 to 0,30	5 ± 0,5
0,30 to 0,50	2,5 ± 0,25

Make sure that valves V-1, V-2, and V-3 are closed.

Set the oven to the optimum heating temperature for the material to be analysed. Wait until the temperature is stabilized.

Weigh to the nearest 0,1 mg a test portion according to the recommendations of Table 3 and transfer this into a sample tube (6.3.2). In case of a powder sample, cover the sample with 2 cm to 3 cm of glass beads (6.3.8). Attach the tube to the instrument. Perform the weighing and attachment procedures as quickly as possible, to avoid moisture release or pick-up.

Open valve V-1 and then V-2. Wait until the pressure indicates a value < 100 Pa. Close valve V-1. Wait for the pressure to stabilize (typically 15 s to 30 s) and record the blank pressure, P_0, on the pressure indicator. Raise the oven until the sample tube is completely inserted in the oven. Wait until the pressure has reached the stop criterion (e.g. ΔP is < 8 Pa/5 min). Record the pressure, *P*, on the pressure indicator.

Close valve V-2 and open valve V-1 to remove the vaporized water until the pressure is < 100 Pa. Close valve V-1 and V-2 and gradually open valve V-3. Air is introduced into the system until atmospheric pressure. Lower the oven. The sample tube can now be removed from the system. Close valve V-3.