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## Plastics — Determination of water content

*Plastiques — Dosage de l'eau*

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# Contents

Page

|                                                                    |           |
|--------------------------------------------------------------------|-----------|
| <b>Foreword</b>                                                    | <b>v</b>  |
| <b>Introduction</b>                                                | <b>vi</b> |
| <b>1 Scope</b>                                                     | <b>1</b>  |
| <b>2 Normative references</b>                                      | <b>2</b>  |
| <b>3 Terms and definitions</b>                                     | <b>2</b>  |
| <b>4 Method A — Extraction with anhydrous methanol</b>             | <b>2</b>  |
| 4.1 Principle                                                      | 2         |
| 4.2 Reagents                                                       | 2         |
| 4.3 Apparatus                                                      | 2         |
| 4.4 Preparation of test sample                                     | 3         |
| 4.4.1 Granules or powder                                           | 3         |
| 4.4.2 Finished articles                                            | 3         |
| 4.5 Procedure                                                      | 3         |
| 4.5.1 Precautions                                                  | 3         |
| 4.5.2 Preparation of test portions                                 | 3         |
| 4.5.3 Determination                                                | 3         |
| 4.6 Expression of results                                          | 4         |
| 4.7 Precision                                                      | 4         |
| <b>5 Method B1 — Water vaporization using a heating tube oven</b>  | <b>4</b>  |
| 5.1 Principle                                                      | 4         |
| 5.2 Reagents                                                       | 4         |
| 5.3 Apparatus                                                      | 5         |
| 5.4 Preparation of test sample                                     | 7         |
| 5.5 Procedure                                                      | 7         |
| 5.5.1 Precautions                                                  | 7         |
| 5.5.2 Preparation of apparatus                                     | 7         |
| 5.5.3 Equipment checks                                             | 7         |
| 5.5.4 Determination                                                | 8         |
| 5.6 Expression of results                                          | 8         |
| 5.7 Precision                                                      | 9         |
| <b>6 Method B2 — Water vaporization using a heated sample vial</b> | <b>9</b>  |
| 6.1 Principle                                                      | 9         |
| 6.2 Reagents                                                       | 9         |
| 6.3 Apparatus                                                      | 10        |
| 6.4 Preparation of test sample                                     | 11        |
| 6.5 Procedure                                                      | 12        |
| 6.5.1 Preparation of apparatus                                     | 12        |
| 6.5.2 Equipment check                                              | 12        |
| 6.5.3 Determination                                                | 12        |
| 6.6 Expression of results                                          | 14        |
| 6.7 Precision                                                      | 14        |
| <b>7 Method C — Manometric method</b>                              | <b>15</b> |
| 7.1 Principle                                                      | 15        |
| 7.2 Reagents                                                       | 15        |
| 7.3 Apparatus                                                      | 15        |
| 7.4 Preparation of test sample                                     | 16        |
| 7.5 Procedure                                                      | 16        |
| 7.5.1 Equipment                                                    | 16        |
| 7.5.2 Outgassing                                                   | 17        |
| 7.5.3 Calibration                                                  | 17        |
| 7.5.4 Determination                                                | 19        |
| 7.6 Expression of results                                          | 20        |

|           |                                                                                                                                      |           |
|-----------|--------------------------------------------------------------------------------------------------------------------------------------|-----------|
| 7.7       | Precision .....                                                                                                                      | 20        |
| <b>8</b>  | <b>Method D — Water detection by using a diphosphorus pentoxide cell .....</b>                                                       | <b>20</b> |
| 8.1       | Principle .....                                                                                                                      | 20        |
| 8.2       | Reagents .....                                                                                                                       | 21        |
| 8.3       | Apparatus .....                                                                                                                      | 21        |
| 8.4       | Preparation of test sample .....                                                                                                     | 22        |
| 8.5       | Procedure .....                                                                                                                      | 23        |
| 8.5.1     | Preparation of apparatus .....                                                                                                       | 23        |
| 8.5.2     | Rinsing the system .....                                                                                                             | 23        |
| 8.5.3     | Tare measurement .....                                                                                                               | 23        |
| 8.5.4     | Cell factor .....                                                                                                                    | 23        |
| 8.5.5     | Equipment check .....                                                                                                                | 23        |
| 8.5.6     | Determination .....                                                                                                                  | 24        |
| 8.6       | Expression of results .....                                                                                                          | 24        |
| 8.7       | Precision .....                                                                                                                      | 25        |
| <b>9</b>  | <b>Method E — Determination of water content by calcium hydride method .....</b>                                                     | <b>25</b> |
| 9.1       | Principle .....                                                                                                                      | 25        |
| 9.2       | Reagents .....                                                                                                                       | 26        |
| 9.3       | Apparatus .....                                                                                                                      | 26        |
| 9.4       | Preparation of test sample .....                                                                                                     | 27        |
| 9.5       | Procedure .....                                                                                                                      | 27        |
| 9.5.1     | Equipment check .....                                                                                                                | 27        |
| 9.5.2     | Calibration .....                                                                                                                    | 28        |
| 9.5.3     | Determination .....                                                                                                                  | 28        |
| 9.5.4     | Expression of results .....                                                                                                          | 29        |
| 9.6       | Precision .....                                                                                                                      | 29        |
| <b>10</b> | <b>Test report .....</b>                                                                                                             | <b>29</b> |
|           | <b>Annex A (informative) Alternative sample preparation methods and titration methods .....</b>                                      | <b>30</b> |
|           | <b>Annex B (informative) Selection of the optimum heating temperature and heating time for the water content determination .....</b> | <b>31</b> |
|           | <b>Annex C (normative) Determination of the water content of a water standard .....</b>                                              | <b>33</b> |
|           | <b>Bibliography .....</b>                                                                                                            | <b>34</b> |

## 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](http://www.iso.org/directives)).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see [www.iso.org/patents](http://www.iso.org/patents)).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see [www.iso.org/iso/foreword.html](http://www.iso.org/iso/foreword.html).

This document was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*.

This fifth edition cancels and replaces the fourth edition (ISO 15512:2016), which has been technically revised. The main change compared to the previous edition is as follows:

- addition of two alternative methods for water determination (Methods D and E).

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at [www.iso.org/members.html](http://www.iso.org/members.html).

## 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 should, 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 document is intended to be followed strictly.

The temperature settings for the vaporization method are not specified in this document. 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 needs to be optimized depending on 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 document, 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.

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# Plastics — Determination of water content

## 1 Scope

This document 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 %. Method D is suitable for the determination of water content as low as 0,01 % with an accuracy of 0,01 %. Method E is suitable for the determination of water content as low as 0,001 % with an accuracy of 0,001 %. The stated accuracies are detection limits which depend also on the maximal possible sample mass. The water content is expressed as a percentage mass fraction of water.

Method D is suitable for polyamide (PA), polycarbonate (PC), polypropylene (PP), polyethylene (PE), epoxy resin, polyethylene terephthalate (PET), polyester, polytetrafluoroethylene (PTFE), polyvinyl chloride (PVC), polylactide (PLA), polyamidimid (PAI), it is especially not recommended for samples which can release  $\text{NH}_3$ . Methods A, B, C and E are generally suitable for all types of plastic and moisture level.

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

Six alternative methods are specified in this document.

- **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  $4 \text{ mm} \times 4 \text{ mm} \times 3 \text{ mm}$ . 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 or a coulometric determination by means of a moisture sensor of the collected water. It can be used for all plastics and is applicable to granules smaller than  $4 \text{ mm} \times 4 \text{ mm} \times 3 \text{ mm}$ .
- **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  $4 \text{ mm} \times 4 \text{ mm} \times 3 \text{ mm}$ .
- **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.
- **Method D** is a thermocoulometric method using a diphosphorus pentoxide ( $\text{P}_2\text{O}_5$ ) cell for the detection of the vaporized water. The water contained in the test portion is vaporized and carried to the sensor cell by a dry air or nitrogen carrier gas, followed by a coulometric determination of the collected water. 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. This is specially related to volatile components which can react with the acidic coating of the diphosphorus pentoxide sensor, e.g. ammonia or any kind of amines. Checks for the presence of large amounts of volatile compounds are to be carried out periodically. Such checks are particularly required for new types or grades of material.

- **Method E** is a calcium hydride based method. The water content of a sample evaporates due to a combination of vacuum and heating. The evaporated water reacts with calcium hydride to molecular hydrogen and calcium hydroxide. The hydrogen causes an increase of pressure in the vacuum that is proportional to the evaporated water. Volatile components, that do not react with calcium hydride condensate in a cooling trap and do not affect the measurement.

## 2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. 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 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

## 4 Method A — Extraction with anhydrous methanol

### 4.1 Principle

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

### 4.2 Reagents

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

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

**4.2.2 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.

### 4.3 Apparatus

Ordinary laboratory apparatus and the following.

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

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

**4.3.3 Reflux condensers**, with ground neck capable of being fitted on to the flasks (4.3.2) and on to the tubes (4.3.4).

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

**4.3.5 Heaters**, suitable for the conical titration flasks (4.3.2).

**4.3.6 Desiccator**, containing a suitable desiccant.

**4.3.7 Analytical balance**, accurate to 0,2 mg.

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

## **4.4 Preparation of test sample**

### **4.4.1 Granules or powder**

Take a representative sample of approximately 100 g. Put the sample into a pre-dried glass flask (4.3.1) and immediately close it with a stopper.

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

### **4.4.2 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.

## **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 test portions**

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.

### **4.5.3 Determination**

Carefully dry the apparatus.

Weigh each test portion to the nearest 1 mg into a conical titration flask (4.3.2) fitted with a ground-glass stopper. Pipette 50 ml of anhydrous methanol (4.2.1) 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 (4.3.6) pending continuation of the test.

Unstopper the flasks and quickly attach them to reflux condensers (4.3.3) fitted with calcium chloride tubes (4.3.4). 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 (4.3.8) to titrate the contents of each flask with Karl Fischer reagent (4.2.2).

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

#### 4.6 Expression of results

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

$$w = \frac{(V_1 - V_2) \cdot T}{m} \cdot 100 \quad (1)$$

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 Formula (1) simplifies to  $V \times T$ .

#### 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.

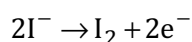
### 5 Method B1 — Water vaporization using a heating tube oven

#### 5.1 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:



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



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

#### 5.2 Reagents

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

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

**5.2.5 Nitrogen gas** ( $N_2$ ), containing less than 5  $\mu\text{g/g}$  of water.

### 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 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 can require a diaphragm for the best possible accuracy. This can be checked with the equipment supplier.

**5.3.2 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.

**5.3.3 Microsyringe**, with capacity of 10  $\mu\text{l}$ , calibrated.

**5.3.4 Sample boat.**

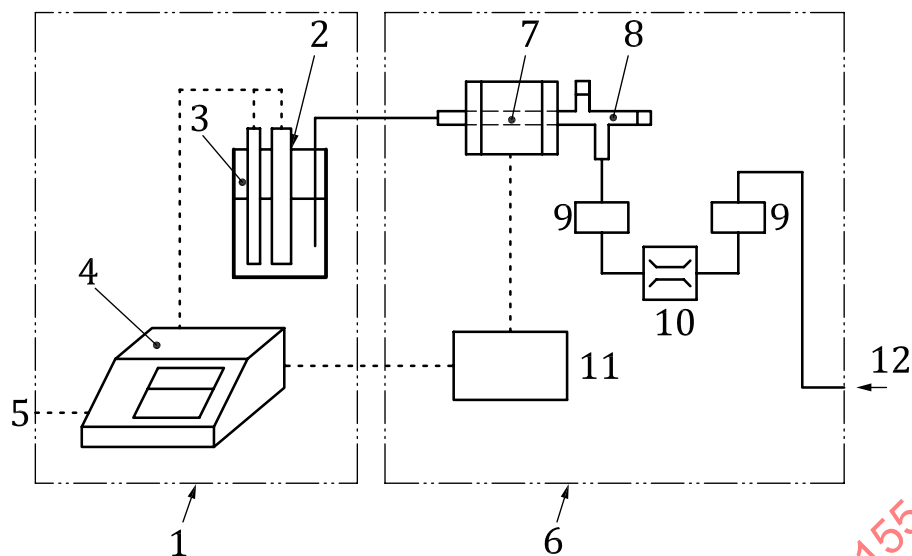
Aluminium foil can be used to hand-fashion a disposable boat large enough to contain the sample and small enough to fit into the heating tube.

**5.3.5 Suitable desiccant**, for the carrier-gas drying tubes ([5.3.2](#)).

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

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

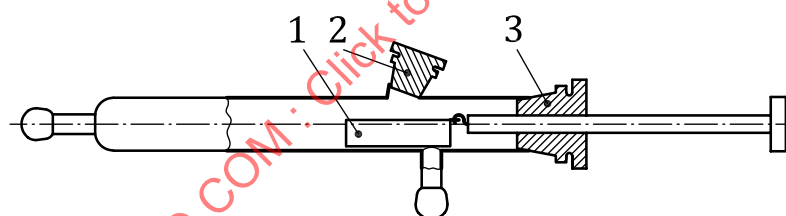
Alternatively, grease, containing little or no water and having low water absorptivity, can be used.



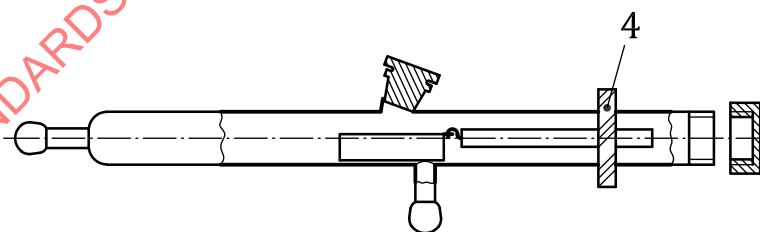
**Key**

- |                                  |                                                                         |
|----------------------------------|-------------------------------------------------------------------------|
| 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**

## 5.4 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.

## 5.5 Procedure

### 5.5.1 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.

### 5.5.2 Preparation of apparatus

Refer to [Figure 1](#) for the following procedure.

Assemble the water vaporizer ([5.3.2](#)) and coulometric Karl Fischer titrator ([5.3.1](#)) as directed in the manufacturer's instructions. Fill the absorption tubes with desiccating agent ([5.3.2](#)) as directed in the manufacturer's instructions.

Pour approximately 200 ml (adjust for the container size) of the anode solution ([5.2.1](#)) into the generator cell and approximately 10 ml of the cathode solution ([5.2.2](#)) into the cathode solution cell ([5.3.1](#)) (adjust these amounts for the container size). 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.

Start the titration cell. If the cell potential shows a negative value, indicating that the anode solution contains an excess of iodine, add 50 µl to 200 µl (adjust for the container size) of the neutralization solution ([5.2.4](#)).

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 ([5.3.2](#)).

Remove any residual water from the walls e.g. by gently swirling the cell. If possible, stir the solution for 1 min 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.

### 5.5.3 Equipment checks

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, start the titration process and carefully inject 5 µl of distilled water into the cell using a 10 µl syringe ([5.3.3](#)). When the titration process is finished, 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 any available certified water standard for Karl Fischer ovens. Examples are:

— sodium tartrate dihydrate with 15,6 % ± 0,5 % water content;

- potassium tartrate hemihydrate with  $3,8 \% \pm 0,2 \%$  water content;
- sodium tungstate diluted for  $1,00 \% \pm 0,03 \%$ .

#### 5.5.4 Determination

Heat the oven to the desired temperature and place the sample boat (5.3.4) 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 needs 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 (5.4) directly into the sample boat (which shall be removed from the heating tube for this purpose) or on to a piece of aluminium foil (see next paragraph). Appropriate masses 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<br>$w$<br>% mass fraction | Mass of test portion<br>$m$<br>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 ready for the measurement. Start the titration process. Move the sample boat into the oven (see Figure 2). Allow the titration process to proceed until finished and then record the instrument reading in micrograms.

#### 5.6 Expression of results

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

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

where

$m_{\text{water}}$  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.

## 5.7 Precision

Interlaboratory data show that a precision of better than 3 % (coefficient of variation) can be achieved with this method.

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

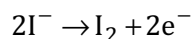
## 6 Method B2 — Water vaporization using a heated sample vial

### 6.1 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:



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



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

### 6.2 Reagents

Only reagents of recognized analytical grade shall be used.

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

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

**6.2.3 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.

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

**6.2.5 Water standard 1 %**, inorganic substance, water content 1 % (mass fraction), every lot individually certified.

**NOTE** The water content can be verified with the method given in [Annex C](#).

**6.2.6 Nitrogen gas (N<sub>2</sub>)**, flow of ≥60 cm<sup>3</sup>/min and preferably containing less than 1 mg/m<sup>3</sup> of water (dew point −80 °C).

NOTE 1 A nitrogen flow of 60 cm<sup>3</sup>/min with a water concentration of 1 mg/m<sup>3</sup> corresponds with a water contribution to the titration cell of 0,06 µg H<sub>2</sub>O/min.

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

### 6.3 Apparatus

Ordinary laboratory apparatus and the following.

**6.3.1 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<sub>2</sub>O/min and a stop criterion of <5 µg H<sub>2</sub>O/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 can be required for the best possible accuracy.

NOTE 2 The start criterion of <20 µg H<sub>2</sub>O/min and the stop criterion of <5 µg H<sub>2</sub>O/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.

**6.3.2 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.

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

**6.3.4 Water vaporizer**, consisting of an oven or a heating device capable of heating a test portion in a sample vial ([6.3.5](#)) to at least 300 °C, a temperature control unit, carrier gas, drying tubes containing a molecular sieve, and a carrier gas flow meter. Vaporizers with higher temperature limit may be used if provided by the manufacturer.

**6.3.5 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.

**6.3.6 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.

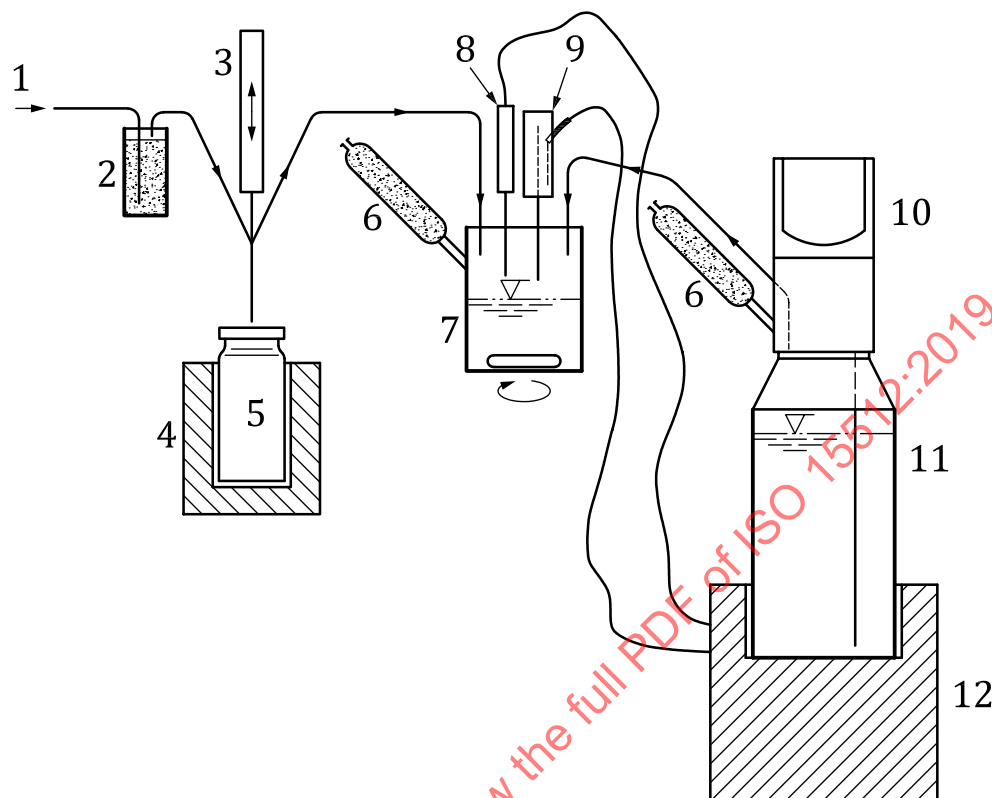
**6.3.7 Analytical balance**, accurate to 0,1 mg.

**6.3.8 Drying oven**, temperature 105 °C.

**6.3.9 Desiccator**, containing an efficient desiccant like molecular sieve or silica gel.

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

**6.3.11 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**

## 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 the glass flasks (6.3.10) and the aluminium foil seal bags (6.3.11) at a temperature of 105 °C in a drying oven (6.3.8) for 1 h. Cool and store in a desiccator (6.3.9).

Take a representative test sample of  $\geq 100$  g, bring it 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  $\times$  4 mm  $\times$  3 mm. Other samples shall be cut to approximately the same size as granules.

## 6.5 Procedure

### 6.5.1 Preparation of apparatus

Prepare the instrument in accordance with the equipment instructions.

Transfer 100 ml to 150 ml of universal single anode reagent (6.2.3) into the titration vessel and immediately close the vessel.

Set the water vaporizer (6.3.4) 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 needs 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 (6.3.5) and immediately close it with an aluminium crimp cap (6.3.6). Place the sample vial in the water vaporizer and start the titration.

Allow the titration to proceed until the release of water is  $<20 \mu\text{g H}_2\text{O}/\text{min}$ . 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 shall 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.

### 6.5.2 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 (6.2.5), using the temperature as given in the certificate of the supplier (150 °C to 200 °C). The result shall be within the certified value  $\pm 0,03 \text{ \% H}_2\text{O}$ .

### 6.5.3 Determination

#### 6.5.3.1 Sample

Select the mass of test portion according the expected moisture content (see Table 2). The sample mass with its absolute mass of water shall 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 0,2 g of sample.

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

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

**Table 2 — Recommended mass of test portion**

| Expected water content<br>$w$<br>% mass fraction | Mass of test portion<br>$m$<br>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 (6.3.5) on an analytical balance (6.3.7). 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 (6.3.6).

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 (6.3.4) 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  $20 \mu\text{g H}_2\text{O}/\text{min}$  (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 (6.2.6) 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  $<Sd_s + \text{stop criterion}$  (see Note). Record the instrument reading ( $m_s$ ) in micrograms  $\text{H}_2\text{O}$  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  $<20 \mu\text{g H}_2\text{O}/\text{min}$  and the start drift corresponds to, e.g.  $17 \mu\text{g H}_2\text{O}/\text{min}$ , the instrument is ready to start. The stop criterion is set to, e.g.  $<5 \mu\text{g H}_2\text{O}/\text{min}$ . 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  $17 + 5 = 22 \mu\text{g H}_2\text{O}/\text{min}$ . If for example the water determination has taken 6 min, the determined quantity of water has to be subtracted by  $6 \times 17 = 102 \mu\text{g H}_2\text{O}$ . This correction procedure applies to both sample and blank.

A start criterion of  $<20 \mu\text{g H}_2\text{O}/\text{min}$  and a stop criterion of  $<5 \mu\text{g H}_2\text{O}/\text{min}$  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 % (mass fraction) water, is analysed and the actual start drift of that determination is  $17 \mu\text{g H}_2\text{O}/\text{min}$ . If the determination takes 12 min, the determined absolute water quantity has to be corrected for  $204 \mu\text{g H}_2\text{O}$ . The sample contains  $600 \mu\text{g H}_2\text{O}$ . In general, the correction value should be a fraction of the water quantity in the sample. As a general rule, the correction value shall 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.  $0,1 \times 600 \mu\text{g H}_2\text{O}/12 \text{ min} = < 5 \mu\text{g H}_2\text{O}/\text{min}$ .

### 6.5.3.2 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  $20 \mu\text{g H}_2\text{O}/\text{min}$  (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 (6.2.6) 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  $<(Sd_{bl} + \text{stop criterion})$ . 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  $(23 \pm 2) ^\circ C$  and  $(50 \pm 10) \%$  relative humidity standard atmosphere, blank values are typically  $80 \mu g H_2O$  to  $100 \mu g H_2O$ . Replicate determinations are expected to have a maximum variation of  $\pm 5 \mu g H_2O$  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.

## 6.6 Expression of results

To obtain a statistic relevant result at least 3 calibrations using a standard shall be performed.

Calculate the mean value of the blank ( $m'_{bl}$ ) using [Formula \(3\)](#).

$$m'_{bl} = \frac{\sum [m_{bl} - (t_{bl} \cdot Sd_{bl})]}{n} \quad (3)$$

where

$m_{bl}$  is the mass of water released during the blank determination, in  $\mu g H_2O$ ;

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

$Sd_{bl}$  is the start drift blank, in  $\mu g H_2O/min$ ;

$n$  is the number of blank determinations.

Calculate the water content of the test sample expressed as a percentage mass fraction using [Formula \(4\)](#).

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

where

$m_s$  is the mass of water released from the test portion, in  $\mu g H_2O$ ;

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

$Sd_s$  is the start drift sample, in  $\mu g H_2O/min$ ;

$m'_{bl}$  is the mean of the blank determinations, in  $\mu g H_2O$ ;

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

## 6.7 Precision

Interlaboratory data show that a precision of better than 3 % (coefficient of variation) can be achieved with this method.

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

## 7 Method C — Manometric method

### 7.1 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.

### 7.2 Reagents

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

The following materials are recommended:

- sodium molybdate dihydrate ( $\text{Na}_2\text{MoO}_4 \cdot 2 \text{H}_2\text{O}$ ), analytical grade, theoretical water content 14,9 % (mass fraction). The actual water content shall be determined according to [Annex C](#).
- water standard 1 % inorganic substance, water content 1 % (mass fraction), every lot individually certified.

NOTE If necessary, the water content can be verified with the method given in [Annex C](#).

### 7.3 Apparatus

Ordinary laboratory equipment and the following.

#### 7.3.1 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  $\pm 0,5$  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  $(\Delta P) < 8 \text{ Pa/5 min}$ .

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

NOTE 2 The stop criterion,  $(\Delta P) < 8 \text{ Pa/5 min}$ , is a default value, applicable for many plastic materials, but can be adjusted when necessary.

**7.3.2 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.

**7.3.3 Drying oven**, temperature 105 °C.

**7.3.4 Desiccator**, containing an efficient desiccant.

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

**7.3.6 Aluminium foil seal bags**, approximately 250 g capacity.

**7.3.7 Analytical balance**, accurate to 0,1 mg.

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

**7.3.9 Aluminium foil.**

## 7.4 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 ([7.3.5](#)) and aluminium foil seal bags ([7.3.6](#)) in a drying oven ([7.3.3](#)). Cool and store in a desiccator ([7.3.4](#)).

Take a representative test sample of  $\geq 100$  g, bring it 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.

## 7.5 Procedure

### 7.5.1 Equipment

#### 7.5.1.1 General

Many modern instruments operate fully automatically or half-automatically. For (half-) automatically operating instruments, the step-by-step instructions described in [7.5.1.2](#), [7.5.2](#), and [7.5.3](#) are not relevant. However, the instrument settings and requirements mentioned in these subclauses, as e.g. the airtight requirement in [7.5.1.2](#), are mandatory.

For manually operated instruments or further detailed information regarding the procedure, see the relevant step-by-step instructions described in [7.5.1.2](#) to [7.5.4](#).

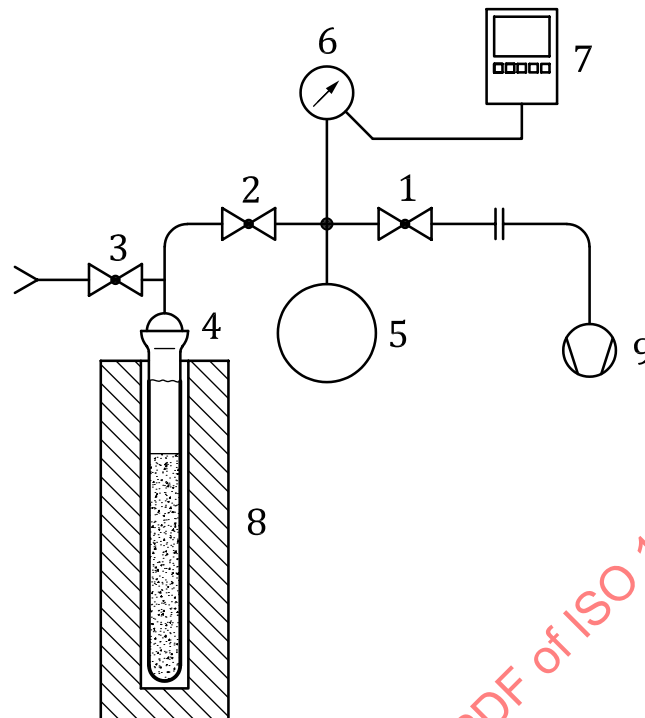
#### 7.5.1.2 Equipment check

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 ([7.3.2](#)) 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 [7.5.2](#)).

**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 $< \pm 1\text{ }^{\circ}\text{C}$ |
| 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**

### 7.5.2 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 (7.3.2) 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  $<100\text{ Pa}$ . 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.

### 7.5.3 Calibration

#### 7.5.3.1 Equipment setup

Set the oven to a temperature of  $190\text{ }^{\circ}\text{C}$ . Wait until the temperature is stabilized.

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

### 7.5.3.2 Water standard preparation — Sodium molybdate dihydrate

Fold a piece of aluminium foil (7.3.9) 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 (7.3.4).

Bring into the aluminium cylinder a quantity of 75 mg to 125 mg sodium molybdate dihydrate (7.2.1) 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 (7.3.2), and immediately attach the tube to the instrument.

Determine the calibration factor following the procedure in 7.5.3.4.

### 7.5.3.3 Water standard preparation — Inorganic substance

Weigh, to the nearest 0,1 mg, 500 mg to 1 000 mg water standard (7.2.1) in a dry sample tube (7.3.2), cover the material with 2 cm to 3 cm of dry glass beads (7.3.8), and immediately attach the tube to the instrument.

Determine the calibration factor following the procedure in 7.5.3.4.

### 7.5.3.4 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<sub>2</sub>O/Pa, using Formula (5).

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

where

$f$  is the instrument calibration factor, in mg H<sub>2</sub>O/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 fraction;

$P$  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  $\pm 0,5$  l, a typical value for the calibration factor,  $f$ , is approximately  $0,005\ 5\ \text{mg H}_2\text{O}/\text{Pa}$ . 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.  $<8\ \text{Pa}/5\ \text{min}$  (stop criterion  $\Delta P$ ). A maximum vaporization time is used to stop the determination when the stop criterion cannot be met within a specified time.

#### 7.5.4 Determination

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

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

In case 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 — Recommended mass of test portion**

| Expected water content<br>% mass fraction | Mass of test portion<br>g |
|-------------------------------------------|---------------------------|
| $<0,075$                                  | $16 \pm 1$                |
| $0,075\ \text{to}\ 0,15$                  | $10 \pm 1$                |
| $0,15\ \text{to}\ 0,30$                   | $5 \pm 0,5$               |
| $0,30\ \text{to}\ 0,50$                   | $2,5 \pm 0,25$            |

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 it into a sample tube ([7.3.2](#)). In case of a powder sample, cover the sample with 2 cm to 3 cm of glass beads ([7.3.8](#)). 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  $<100\ \text{Pa}$ . 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.  $\Delta P < 8\ \text{Pa}/5\ \text{min}$ ). 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  $<100\ \text{Pa}$ . 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.

## 7.6 Expression of results

Calculate the water content of the test sample expressed as a percentage mass fraction using [Formula \(6\)](#).

$$w = \frac{(P - P_0) \cdot f}{m \times 10} \quad (6)$$

where

$P$  is the pressure after completion of the water vaporization, in pascals;

$P_0$  is the pressure at the start of the determination, in pascals;

$f$  is the instrument calibration factor, in mg H<sub>2</sub>O/Pa;

$m$  is the mass of the test sample, in grams.

At a pressure of approximately 2 300 Pa water starts to condensate. It is recommended a sample quantity be selected such that the pressure at the completion of the water vaporization is between 500 Pa and 2 000 Pa.

## 7.7 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.

# 8 Method D — Water detection by using a diphosphorus pentoxide cell

## 8.1 Principle

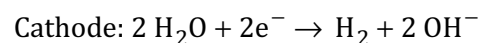
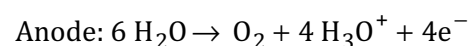
The test portion is weighed into a sample container and heated to a specific temperature. The water contained in the sample is vaporized and carried to a diphosphorus pentoxide cell by a stream of dry air or nitrogen carrier gas. The electrochemical diphosphorus pentoxide sensor detects the water selectively.

The method belongs to the field of thermo-coulometric determination. In thermo-coulometric determination the quantity of electric charge is measured which is required to completely electrolyze (dissociate) a substance. If the charge that flowed during electrolysis is known, using the Faraday's law, it is possible to calculate the magnitude of the original mass of the substance under examination.

The chemical reaction of the water released by thermal means and subsequent detection with diphosphorus pentoxide causes the electrolytic dissociation of the water molecules as follows:



Electrolysis of water molecules



The absorbed water molecules are electrolyzed, i.e. they are broken down into their components, hydrogen and oxygen and thereafter conveyed out of the measuring system by the carrier gas. Two electrons from each electrolyzed water molecule contribute to a measurable electric current. The

measured electric current is directly linked to the number of detected water molecules and therefore to the volume of the water evaporated out of the sample via Faraday's law.

Due to possible reactions of  $P_2O_5$  with  $NH_3$ , amines and alcohols, one shall be sure that none of these compounds are released when the sample is heated up.

## 8.2 Reagents

Only reagents of recognized analytical grade shall be used.

**8.2.1 Coating solution**, containing phosphorus acid to generate  $P_2O_5$ , in accordance with the equipment manufacturer's instructions.

**8.2.2 Water standard 1 %**, inorganic substance, water content 1 % (mass fraction), every lot individually certified.

NOTE The water content can be verified with the method given in [Annex C](#).

**8.2.3 Nitrogen gas ( $N_2$ )**, flow of  $\leq 80$  ml/min and preferably containing  $\leq 5$  ppm (parts per million) of water (dew point  $-80$  °C) as a minor component. The initial gas pressure shall be  $< 0,5$  bar.

NOTE Value of water content of nitrogen is to be understood as the mole fraction (mol %, ppm).

## 8.3 Apparatus

Ordinary laboratory apparatus and the following.

**8.3.1 Thermocoulometric water determination using diphosphorus pentoxide cell**, consisting of an electric oven with adjustable temperatures, a control unit and a sensor-cell assembly equipped with an electrochemical diphosphorus pentoxide sensor.

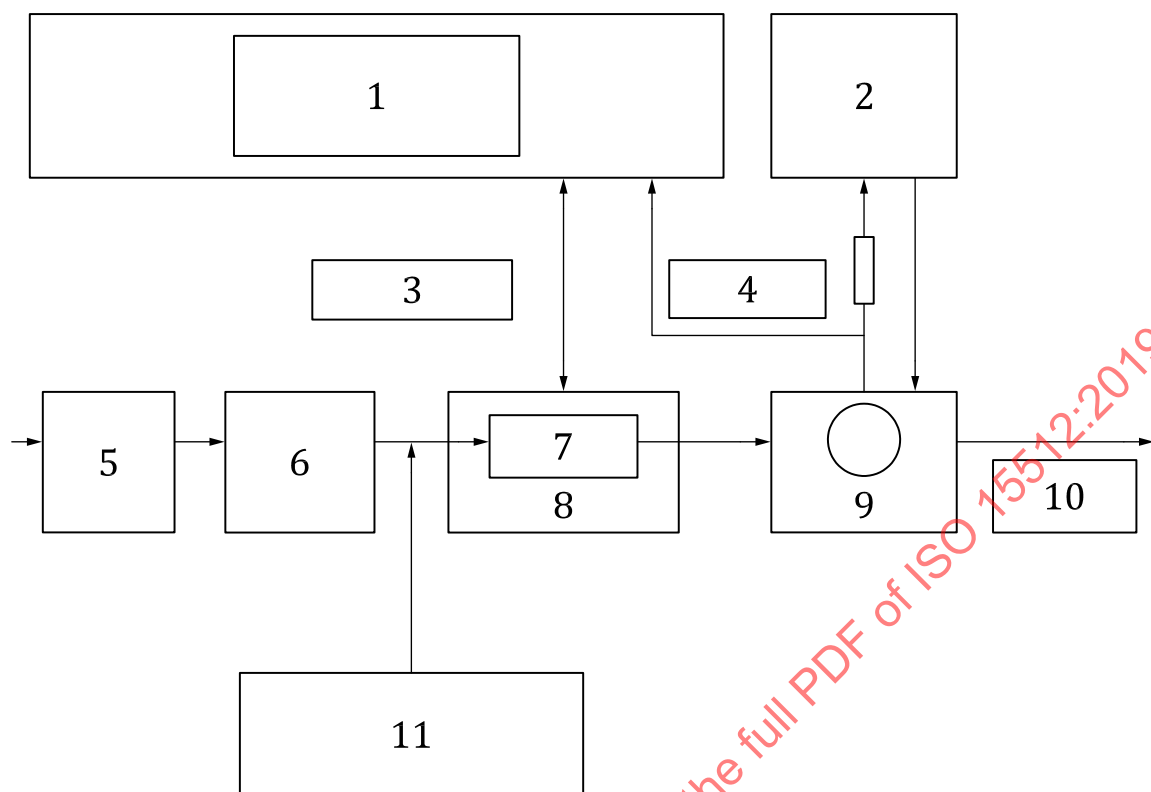
The basic structure of the measuring cell consists of two electrodes parallel to each other, with a thin layer of diphosphorus pentoxide between the two electrodes. The water released from the sample by thermal means is transported by the carrier gas piped through the system to the electrochemical sensor. The gas, loaded with the sample water, flows over the diphosphorus pentoxide layer which is extremely hygroscopic and ideally completely absorbs the water molecules.

The analyser for the water determination using diphosphorus pentoxide cell is schematically shown in [Figure 5](#).

**8.3.2 Sample container**, according to manufacturer's instructions.

**8.3.3 Molecular sieve**,  $10 \text{ \AA}$ , 1,6 mm to 2,5 mm spherical molecular sieve.

**8.3.4 Analytical balance**, accurate to 0,1 mg.



**Key**

- 1 controller data evaluation
- 2 power supply, 50 V DC
- 3 temperature
- 4 current signal
- 5 air pump
- 6 gas dryer
- 7 sample
- 8 oven
- 9 sensor
- 10 exhaust
- 11 N<sub>2</sub> gas supply (optional)

**Figure 5 — System setup for the determination of water according to method D — Schematic**

**8.4 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.

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.

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

## 8.5 Procedure

### 8.5.1 Preparation of apparatus

Prepare the instrument in accordance with the manufacturer's instructions.

### 8.5.2 Rinsing the system

The system should be thoroughly rinsed with dry gas prior to the first measurement. The measuring current should be stable and lower than 0,5 mA before beginning to measure.

### 8.5.3 Tare measurement

A tare measurement, i.e. a measurement of the entire background during a measuring process shall be performed in order to correct both external (air humidity, sample handling) and internal influences (moisture content of the carrier gas, electronic offset). The tare measurement shall be used for the background correction of the sample analyses for all subsequent analyses until a new tare measurement is recorded.

The tare measurement shall be performed as far as possible in the same manner as the actual measurement, only without any sample in the sample container. Therefore, an identical temperature profile shall be selected. The test laboratory shall use a fixed schedule of tare measurements to ensure continuous validity of the test results, e.g. one tare measurement before the first sample is measured and another one at least after every 10 samples.

### 8.5.4 Cell factor

The cell factor,  $f$ , is defined as the ratio between a set water content (8.2.2) and the measured water content. See [Formula \(7\)](#).

$$f = \frac{w_{\text{set}}}{w_{\text{det}}} \quad (7)$$

where

$f$  is the instrument cell factor;

$w_{\text{set}}$  is the set water content based on a certified water standard in % mass fraction;

$w_{\text{det}}$  is the determined water content in % mass fraction.

The cell factor can be determined by measuring the water content of the water standard (8.2.2) and shall be used for the evaluating sample analyses and for all subsequent analyses until a new calibration is recorded. The determination of the cell factor shall be performed immediately after tare analysis and in a timely manner before analysing the first sample.

The calibration procedure may be different for different instruments.

The cell factor shall not be greater than 1,3 nor smaller than 0,8.

### 8.5.5 Equipment check

Carry out a water determination in order to check if the equipment is functioning properly by analysing 10 mg to 20 mg of the water standard (8.2.2), using the temperature as given in the certificate of the supplier (150 °C to 200 °C). The result shall be within the certified value  $\pm 0,03$  % H<sub>2</sub>O.

## 8.5.6 Determination

### 8.5.6.1 Sample

Select the mass of test portion according to the expected moisture content (see [Table 4](#)).

Carry out a preliminary determination if the water content of the sample is unknown, using 0,1 g of sample.

In case the composition of the test sample is unknown, select the optimum heating temperature according to material properties, i.e. decomposition or melting temperature.

**Table 4 — Recommended mass of test portion**

| Expected water content<br>$w$<br>% mass fraction | Mass of test portion<br>$m$<br>g |
|--------------------------------------------------|----------------------------------|
| $w > 1$                                          | $m < 0,02$                       |
| $1 \geq w > 0,1$                                 | $0,02 < m \leq 0,2$              |
| $0,1 \geq w > 0,01$                              | $0,2 < m \leq 2$                 |

Place a sample container ([8.3.2](#)) on an analytical balance ([8.3.4](#)). Add the selected test portion (see [Table 4](#)) into the sample container and determine the mass of the test portion ( $m_{\text{test portion}}$ ).

Perform the weighing procedure as quickly as possible to avoid moisture release or pick-up. The sample material should be positioned in the direct vicinity of the instrument and the balance. Shortest possible paths prevent errors which can arise from the evaporation of volatile water fractions or due to the absorption of water in the case of hygroscopic sample material. Carry out the subsequent water determination in a timely manner after weighing.

Check that the background current is below 0,5 mA before starting the analysis.

Set an appropriate temperature program according to sample material properties. Place the sample in the heating device. Start the heating program. The release of water is automatically recorded.

Do not heat samples above their melting temperature because volatilization of uncontrollable chemical compounds, or the denaturation of the sample as a consequence of excessively high temperatures shall be avoided.

The end point of the water determination is reached if one of the following criteria is fulfilled:

- minimum analysis time;

EXAMPLE If a minimum analysis time of 10 min is selected, the analysis runs until the 10 min ends.

- switch-off current.

The present measuring current is compared with the switch-off criterion. The measurement is continued until the measuring current drops below the switch-off current value. The analysis is automatically terminated.

EXAMPLE A switch-off current of 0,7 mA is selected. If the measuring current of the analysis reaches a value of minimum 0,69 mA (<0,7 mA) the analysis stops automatically.

## 8.6 Expression of results

Calculate the water content,  $w$ , of the test sample expressed as a percentage mass fraction using [Formula \(8\)](#).

$$m_{\text{abs}} = \frac{f \cdot M}{z \cdot F} \cdot \int I(t) \cdot dt \quad (8)$$

$$w = \frac{m_{\text{abs}}}{m_{\text{test portion}}} \cdot 100 \%$$

where

|                           |                                                                                                     |
|---------------------------|-----------------------------------------------------------------------------------------------------|
| $m_{\text{abs}}$          | is the absolute mass of water in $\mu\text{g}$ ;                                                    |
| $w$                       | is the content of water in % $\text{H}_2\text{O}$ mass fraction;                                    |
| $M$                       | is the molar mass of water = 18,016 g/mol;                                                          |
| $\int I(t) \cdot dt$      | is the integral of the electrical current over time (i.e. the total electrical charge transferred); |
| $z$                       | is the number of released electrons = 2;                                                            |
| $F$                       | is the Faraday constant = 96,484 56 kC/mol;                                                         |
| $m_{\text{test portion}}$ | is the mass of the test portion in $\mu\text{g}$ ;                                                  |
| $f$                       | cell factor.                                                                                        |

## 8.7 Precision

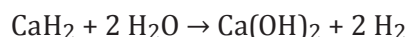
Interlaboratory data show that a precision of better than 3 % (coefficient of variation) can be achieved with this method.

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

## 9 Method E — Determination of water content by calcium hydride method

### 9.1 Principle

The sample is weighed and put into a sample cup. Before the measurement, the sealed reaction vessel is evacuated by using a vacuum pump. This excludes the influence of air humidity and lowers the vapour pressure of water. When the vacuum is reached, the container is heated up to the measuring temperature. The evaporating water reacts with the reagent calcium hydride and generates hydrogen according the following reaction:



The hydrogen increases the pressure proportional to the evaporated water and is monitored by a pressure transducer. 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 1** If the sample includes low molecular weight alcohols, the water content determined by calcium hydride method will be overvalued. Should other components evaporate which also react with calcium hydride, this needs to be considered.

NOTE 2 There is only a small amount of hydrogen produced during a measurement. Before the next measurement, the device is ventilated with ambient air. The gas mixture is not flammable, because of the small amount of hydrogen.

## 9.2 Reagents

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

The use of sodium molybdate dihydrate ( $\text{Na}_2\text{MoO}_4 \cdot 2 \text{H}_2\text{O}$ ), analytical grade, is recommended. The actual water content shall be determined according to [Annex C](#).

**9.2.2 Calcium hydride ( $\text{CaH}_2$ )**, analytical grade.

## 9.3 Apparatus

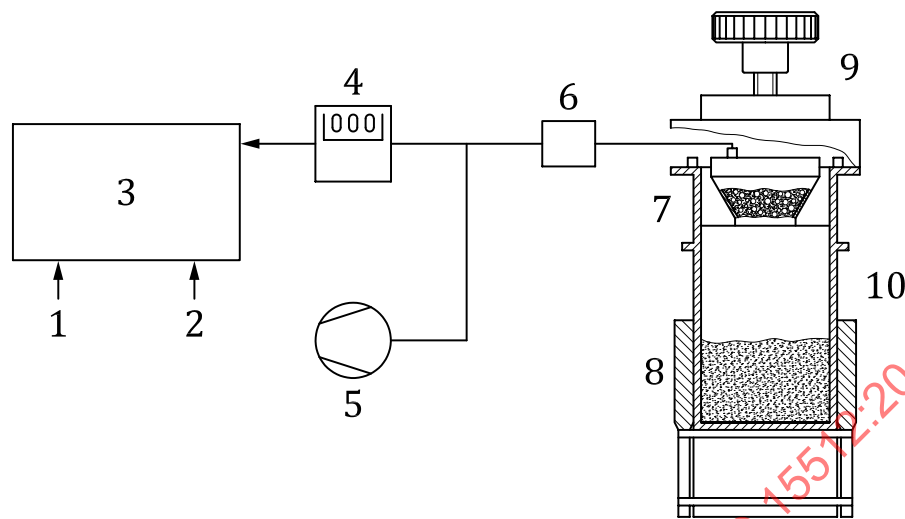
**9.3.1 Calcium hydride moisture measuring instrument**, schematically shown in [Figure 6](#) and consisting of the following.

- **Sample cup**, designed for holding samples and made of stainless steel. Its temperature resistance is 250 °C. A sample cup with a capacity of about 170 ml is recommended.
- **Heating jacket**, temperature control unit with adjustable temperatures between 60 °C and 200 °C. The heating jacket can package the sample cup at least half of the volume.
- **Reactor unit**, reagent insert, designed to be used for holding calcium hydride and made of stainless steel. Approximately 20 ml capacity, the upper part of the reactor unit has small holes, so that the evaporating water reacts with the calcium hydride.
- **Cooling trap**, used to condense volatiles, that do not react with calcium hydride.
- **Vacuum pump**, so that an absolute pressure, smaller than 10 mbar is generated.
- **Measurement cell**, consisting of a pressure transducer.
- **Output unit**: Two types of output units (A or B) are permitted. Type A is a pressure indicator that shows the pressure ( $P$  in  $\text{mbar}^{1)}$ ) with an accuracy of 0,1 mbar; Type B is a display that shows the water content (percentage or ppm) directly with an accuracy of 0,001 %. The output unit calculates the water content from the pressure, the temperature and the volume in the measurement area based on the ideal gas equation.

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1) 1 mbar = 100 Pa.

### 9.3.2 Analytical balance, accurate to 0,1 mg.



#### Key

- 1 readout pressure, or
- 2 water content
- 3 output unit
- 4 measurement cell
- 5 vacuum pump
- 6 cooling trap
- 7 reactor unit
- 8 heating jacket
- 9 reactor cover
- 10 sample cup

**Figure 6 — Calcium hydride moisture measuring instrument — Schematic**

## 9.4 Preparation of test sample

The absolute amount of water to be determined is in most cases far below humidity of air. Therefore, maximum care shall be taken to avoid contaminating the sample with water from the sample container, the atmosphere, sample transfer, and/or equipment. The sample should be processed, weighed and transferred quickly in a dry environment or under nitrogen gas (N<sub>2</sub>). Put the sample into a pre-dried glass flask and immediately close it with a stopper.

The material category is not specified in this document and the test sample can be in any form, such as granules, moulding powder, fabricated shapes, or moulded items. The required sample should be cut or sawed into pieces of appropriate size, i.e. having a maximum size of 5 mm × 3 mm × 3 mm, produced as quick as possible to minimize moisture absorption.

## 9.5 Procedure

### 9.5.1 Equipment check

#### a) Leak check

The air tightness of the system is checked automatically by the device with a leak test. Put an empty and clean sample cup into the reaction vessel. By starting the leak test the device is evacuated by the vacuum pump. An absolute pressure, below 10 mbar, is generated and the pressure increase