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Paints and varnishes — Determination of water content — Gas-chromatographic method

Peintures et vernis — Détermination de la teneur en eau — Méthode par chromatographie en phase gazeuse

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Foreword

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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.

This document was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 9, *General test methods for paints and varnishes*.

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.

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Paints and varnishes — Determination of water content — Gas-chromatographic method

1 Scope

This document specifies a method for the determination of the water content of water-borne coating materials and their raw materials by using a gas chromatograph. The preferred working range of this test method is from a water mass fraction of 15 % to a water mass fraction of 90 % but the method can be applied outside of this range.

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)*

ISO 1513, *Paints and varnishes — Examination and preparation of test samples*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 4618, *Paints and varnishes — Terms and definitions*

ISO 15528, *Paints, varnishes and raw materials for paints and varnishes — Sampling*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 4618 and the following apply.

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/

3.1
ready for use
state of a product when it is mixed in accordance with the manufacturer's instructions in the correct proportions and thinned if required using the correct thinners so that it is ready for application by the approved method

[SOURCE: ISO 11890-2:2013, 3.4]

4 Principle

A suitable amount of the sample is internally standardized, diluted with appropriate organic solvent, and then injected into a gas chromatographic column that separates water from other components, after which the water is detected by a thermoconductivity detector and quantified from the peak areas using the internal standard.

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5 Apparatus

5.1 Gas chromatograph

The apparatus shall be set up and used in accordance with the manufacturer's instructions. All of the instrumental parts coming into contact with the test sample shall be made of a material (e.g. glass) which is resistant to the sample and will not change it chemically.

5.2 Sample injection system

The instrument shall have a variable-temperature injection block with a sample splitter. The injection temperature shall be capable of being set to an accuracy of 1 °C. The split ratio shall be adjustable and capable of being monitored. The sample splitter insert shall contain silanized glass wool to retain nonvolatile constituents, and shall be cleaned and provided with new glass wool packing or replaced as required to eliminate errors due to residues of binder or pigment (i.e. adsorption of compounds).

5.3 Oven

The oven shall be capable of being heated between 40 °C and 300 °C both isothermally and under programmed temperature control. It shall be possible to set the oven temperature to within 1 °C. The final temperature of the temperature programme shall not exceed the maximum operating temperature of the column (see 5.5).

5.4 Detector

Thermoconductivity detector (TCD), capable of being operated at temperatures up to 300 °C. The injection volume, split ratio and gain setting shall be optimized so that the signals (peak areas) used for the calculation are proportional to the amount of substance.

5.5 Capillary column

The column shall be made of glass or fused silica. Columns of sufficient length to resolve water and of maximum internal diameter 0,53 mm, based on bonded porous polymer technology shall be used. Columns should also show good stability and reproducibility with samples containing large amounts of water. Other columns proved to be equally suitable may also be used.

5.6 Injection syringe

The injection syringe shall have a capacity of at least twice the volume of the sample to be injected into the gas chromatograph.

5.7 Data processing

A suitable software shall be used for integration, calibration, quantification and other data handling processes.

5.8 Sample vials

Use vials made of chemically inert material (e.g. glass) which can be sealed with a suitable septum cap [e.g. a rubber membrane coated with poly(tetra fluoro ethylene)].

5.9 Gas filter

A filter shall be installed in the gas chromatograph connection pipes to adsorb residual impurities in the gas (see 5.10).

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Care should be taken that any moisture that might be present in the carrier gas is eliminated through the use of a suitable carrier gas purifier. Trace levels of water will accumulate on the column at low oven temperatures and might affect the reproducibility as well as the accuracy of the determination.

5.10 Carrier gas

Hydrogen of 99,995 % or higher purity. High-purity helium may also be used.

5.11 Analytical balance

Capable of weighing to an accuracy of 0,1 mg.

5.12 Bottle-top dispenser

Dispensers shall be equipped with a drying tube. All parts of the dispensers shall be inert to the solvents used.

6 Reagents and materials

During the analysis, use only reagents of recognized analytical grade. Other grades may also be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.1 Internal standard (anhydrous)

The internal standard shall be a compound which is not present in the sample and is completely separated from the other components in the chromatogram. It shall be inert with respect to the sample constituents, stable in the required temperature range, and of known purity. Dry the internal standard with the molecular sieve (6.4). Dispense the internal standard with the bottle-top dispenser (5.12).

NOTE 2-propanol or n-propanol has been found suitable.

6.2 Dilution solvent

Use an organic solvent suitable for diluting the sample. It shall have a purity of at least 99 % (mass fraction) or shall be of known purity, and it shall not contain any substances which interfere with the determination, e.g. causing overlapping peaks in the chromatogram. Always carry out a separate run injecting the solvent alone in order to observe contaminants and possible interference peaks, especially in trace analysis. Dry the dilution solvent with the molecular sieve (6.4). Dispense the dilution solvent with the bottle-top dispenser (5.12).

NOTE Dimethylformamide (DMF) has been found suitable.

6.3 Water

Water conforming to the requirements of grade 3 or higher of ISO 3696 shall be used.

6.4 Molecular sieve

Pore diameter: 2 Å to 3 Å (= 2×10^{-7} mm to 3×10^{-7} mm); particle size: 1,7 mm to 5,0 mm.

The molecular sieve shall be regenerated before use.

7 Sampling

Take a representative sample of the product to be tested (or of each product in the case of a multi-coat system), as specified in ISO 15528.

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Examine and prepare each sample for testing, as specified in ISO 1513, preparing the final sample for testing in the "ready for use" state.

8 Procedure

8.1 Gas-chromatographic conditions

The gas-chromatographic conditions used depend on the product to be analysed and shall be optimized each time using a known calibration mixture. Examples of gas-chromatographic conditions are given in Annex A.

The injection volume and the split ratio shall be coordinated so as not to exceed the capacity of the column and to remain within the linear range of the detector. Asymmetrical peaks will give an indication of overloading of the gas-chromatographic system.

8.2 Water content of the dilution solvent

Determine the water content of the dilution solvent (6.2) by Karl Fischer titration method as described in ISO 760.

8.3 Calibration

The response factor shall be determined using the following technique.

Weigh about 0,4 g of water (6.3) and 0,4 g of internal standard (6.1), to the nearest 0,1 mg, into a sample vial (5.8). Weigh about 10,0 g of dilution solvent (6.2) into the same vial (5.8), to the nearest 0,1 mg. If the dilution solvent (6.2) is anhydrous, simply add 10 ml of it as weighing is not necessary.

Inject 0,1 µl to 1,0 µl of the calibration mixture twice under the conditions specified in 8.1. From each calibration chromatogram, calculate the response factor for water using Formula (1):

$$r_{\mathrm{w}} = \frac{\left(m_{\mathrm{cw}} + m_{\mathrm{ds}} \times P\right) \times A_{\mathrm{is}}}{m_{\mathrm{is}} \times A_{\mathrm{cw}}} \tag{1}$$

where

r_{w} is the response factor for water;

P is the water content, in grams per gram, of the dilution solvent (see 8.2);

m_{ds} is the mass, in grams, of the dilution solvent;

m_{is} is the mass, in grams, of the internal standard in the calibration mixture;

m_{cw} is the mass, in grams, of water intentionally added to the calibration mixture;

A_{is} is the peak area of the internal standard;

A_{cw} is the peak area of water in the calibration mixture.

Calculate the mean value ($\bar{r}_w$) of the two calibration response factors.

8.4 Sample preparation

The mass of the sample depends on the expected water content w (see Table 1).

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Table 1 — Mass of sample

Expected water content, w % (mass fraction)	**Mass of sample** g
$15 \leq w \leq 30$	2,0
$30 < w \leq 50$	1,0
$50 < w \leq 70$	0,7
$70 < w \leq 90$	0,5

Weigh to the nearest 0,1 mg, the sample and about 0,4 g of the internal standard (6.1) into the sample vial (5.8). Weigh about 10,0 g of dilution solvent (6.2) into the same vial (5.8), to the nearest 0,1 mg. If the dilution solvent (6.2) is anhydrous, simply add 10 ml of it as weighing is not necessary. Seal the vial, shake the vials on a wrist action shaker or other suitable device for 15 min. To facilitate setting of solids, allow the vials to stand for a suitable time just prior to injection into the chromatograph. If particles do not readily settle, phase cleaning may be obtained by centrifugation.

NOTE Dry mixing glass beads added to the vials have proved beneficial with viscous samples.

8.5 Quantitative determination of water content

Set the instrumental parameters as specified in 8.1.

Inject 0,1 µl to 1 µl of the "ready for use" sample into the gas chromatograph and record the chromatogram. Determine the peak areas for water and the internal standard. Determine the water content of the sample using Formula (2):

$$w_{sw} = \bar{r}_w \times \frac{m_{is} \times A_{sw}}{m_s \times A_{is}} \times 100 \quad (2)$$

where

w_{sw} is the water content, as a percentage mass fraction, of the sample;

$\bar{r}_w$ is the mean value of the two calibration response factors for water;

m_{is} is the mass, in grams, of the internal standard in the calibration mixture;

m_s is the mass, in grams, of the sample;

A_{is} is the peak area of the internal standard;

A_{sw} is the peak area of water of the test sample.

Repeat the procedure.

If the blank indicates the presence of a detectable peak for water in the solvent (6.2), apply a correction in the calculation by using Formula (3) and Formula (4):

$$w_{dsw} = \frac{m_{ds} \times P}{m_s} \times 100 \quad (3)$$

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where

w_{dsw} is the water content, as a percentage mass fraction, due to the dilution solvent;

m_{ds} is the mass, in grams, of the dilution solvent;

P is the water content, in grams per gram, of the dilution solvent (see 8.2);

m_s is the mass, in grams, of the sample.

$$w_{csw} = w_{sw} - w_{dsw} \quad (4)$$

where

w_{csw} is the water content, as a percentage mass fraction, of the sample by correction;

w_{sw} is the water content, as a percentage mass fraction, of the sample;

w_{dsw} is the water content, as a percentage mass fraction, due to the dilution solvent.

9 Expression of results

If the two results (duplicates) differ by more than the maximum value indicated in 10.2, repeat the procedure. Calculate the mean of two valid results (replicates). Mass fractions shall be reported at least to the nearest 0,1 %.

10 Precision

10.1 General

The precision of the test method was determined by interlaboratory testing in accordance with ISO 5725-1 and ISO 5725-2. Details can be found in Annex B.

10.2 Repeatability limit, *r*

The repeatability limit, *r*, is the value below which the absolute difference between two single test results, each the mean of duplicates, obtained on identical material by one operator in one laboratory within a short interval of time using the standardized test method, may be expected to lie.

The repeatability for four repeated determinations made using this test method, expressed as the repeatability coefficient of variation, lies between 0,2 % and 1,0 %.

10.3 Reproducibility limit, *R*

The reproducibility limit, *R*, is the value below which the absolute difference between two test results, each the mean of duplicates, obtained on identical material by operators in different laboratories using the standardized test method, might be expected to lie.

The reproducibility for this test method, expressed as the reproducibility coefficient of variation, lies between 0,6 % and 3,0 %.

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11 Test report

The test report shall contain at least the following information:

a) all details necessary for complete identification of the tested product (manufacturer, trade name, batch number, etc.);

b) a reference to this document (i.e. ISO 23168:2019);

c) the gas-chromatographic conditions to be used (see 8.1);

d) the results of the test, as indicated in 8.5, and the method of calculation used (see 8.5);

e) the dilution solvent used;

f) any deviation from the test method specified;

g) any unusual features (anomalies) observed during the test;

h) the date of the test.

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Annex A
(informative)

Example of gas-chromatographic conditions

Detector	Thermal conductivity
Column	CP-PoraBond Q[a], bonded with poly(styrene-divinylbenzene), 25 m × 0,53 mm × 10 µm
Injector temperature	250 °C
Detector temperature	300 °C
Programme	Initial temperature: 100 °C First isothermal holding time: 2 min Heating rate: 20 °C/min Second isothermal holding temperature: 130 °C Holding time: 3 min Heating rate: 30 °C/min Final temperature: 200 °C Isothermal holding time: 5 min
Carrier gas	Hydrogen
Flow rate	6,5 ml/min
Injection volume	1 µl
Split ratio	1:5

[a] CP-PoraBond Q is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

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