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Paints and varnishes — Determination of solvents in water-thinnable coating materials — Gas-chromatographic method

Peintures et vernis — Détermination des solvants dans des peintures diluable à l'eau — Méthode par chromatographie en phase gazeuse

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Foreword

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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.

Paints and varnishes — Determination of solvents in water-thinnable coating materials — Gas-chromatographic method

1 Scope

This document specifies a method for the gas-chromatographic determination of the solvents in water-thinnable paints and varnishes, binder solutions, emulsions and dispersions.

With the precision stated in Clause 13, single components above 0,02 % (mass fraction) can be determined quantitatively.

The method defined in this document is not applicable for the determination of Volatile Organic Compounds (VOC) and Semi-Volatile Organic Compounds (SVOC) content.

NOTE For the determination of VOC and SVOC, see ISO 11890-2[2].

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 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 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/

4 Units

The analytical results are expressed as a percentage mass fraction.

5 Principle

After sample preparation, the components contained in the sample under test are separated by gas chromatography. Either a hot or a cold sample injection system can be used, depending on the product type. After the components have been identified, they are quantified from the peak areas using the internal standard method.

6 Apparatus

6.1 Gas chromatograph

6.1.1 General

The gas chromatograph shall be suitable for use with capillary separation columns and meet the conditions specified in 6.1.2 to 6.1.4.

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 which will not change it chemically.

6.1.2 Sample injection system

6.1.2.1 Hot 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 K. The split ratio shall be adjustable and capable of being monitored. The sample splitter insert shall contain silanized glass wool to retain non-volatile constituents. It shall be cleaned and provided with new glass wool packing or replaced as required to rule out errors due to residues of binder or pigment (e.g. adsorption of solvents). The occurrence of adsorption is revealed by peak tailing, in particular with components of low volatility.

6.1.2.2 Cold injection system

The cold injection system shall be provided with temperature programming for heating from room temperature to 300 °C and shall have a sample splitter inlet made of a material such as glass. It shall be provided with a silanized glass wool packing and shall be treated as specified in 6.1.2.1. In this case too, the split ratio shall be adjustable and capable of being monitored.

6.1.2.3 Automatic sample injection system

The precision of the method will be increased if the injection systems, especially the hot injection system, are coupled to an auto injector. The manufacturer's instructions shall be followed when an auto injector is used.

6.1.3 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 K. The final temperature of the temperature program shall not exceed the maximum operating temperature of the separation column (see manufacturer's instructions).

6.1.4 Detector

A Flame Ionization Detector (FID) which is capable of being operated at temperatures up to 300 °C shall be used. To prevent condensation, the detector temperature shall be at least 10 K above the maximum oven temperature. The detector gas supply, 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

If the separated components are identified by a mass spectrometer, mass-selective detector of Fourier-transform infrared spectrometer (FT-IR spectrometer), these instruments shall be coupled to the gas chromatograph and operated in accordance with the manufacturer's instructions.

6.1.5 Capillary separation column

The capillary separation column shall be made of glass or fused silica. To obtain overall chromatograms, use capillary separation columns (for example of length 50 m and internal diameter 0,2 mm) coated with polydimethylsiloxane or poly (ethylene glycol) at a film thickness of e.g. 0,2 µm. The stationary phase and column length shall be varied to suit the particular separation (see examples in 10.1). The resolution, *R*, of the peaks to be separated shall be at least 1,5.

6.1.6 Injection syringe

The injection syringe shall have a capacity between 0,5 µl and 10 µl and shall have 0,1 µl scale divisions.

6.2 Data acquisition

The signals from the detector are recorded by means of an electronic data-acquisition system. The integration parameters used in calibration and analysis shall be identical.

6.3 Sample vessel

A suitable sample vessel is one made of chemically inert material, such as glass, which can be sealed with, for example, a rubber membrane which has a coating of polytetrafluoroethylene (PTFE). The vessel shall be filled to about 90 % of capacity.

7 Reagents

7.1 Gases

7.1.1 Carrier gas, dry oxygen-free helium, nitrogen or hydrogen having a purity of at least 99,996 % (volume fraction).

7.1.2 Detector gases, hydrogen having a purity of at least 99,999 % (volume fraction) and (synthetic) air free of organic compounds.

7.1.3 Auxiliary gas, nitrogen or helium of the same quality as the carrier gas.

Suitable filters shall be installed in the gas chromatograph connection pipes to adsorb residual impurities (see the gas chromatograph operating instructions).

7.2 Internal standard

The internal standard shall be a solvent which is completely separated from the other components, for example, isobutanol, CAS-No 78-83-1[1)] or diethylene glycol dimethyl ether, CAS-No 111-96-6. The internal standard shall be inert with respect to the sample constituents, stable in the required temperature range, and of known purity.

7.3 Calibration substances

The solvent used for the calibration shall have a purity of at least 99 % (mass fraction) or shall be of known purity.

7.4 Diluents

Organic diluents such as methanol, CAS-No 67-56-1, or tetrahydrofuran, CAS-No 109-99-9, are suitable for diluting the sample. The diluents shall have a purity of at least 99 % (mass fraction) or be of known

1) CAS-No: Chemical Abstracts Service Registry Number.

purity and shall not contain any substances which interfere with the determination by for example causing overlapping peaks in the chromatogram.

8 Sampling

Take a representative sample, as described in ISO 15528.

9 Choice of sample injection system

The choice between hot injection and cold injection will depend on the type of product under test. It is necessary to use the cold injection system for products which, at high temperature, release substances which interfere with the determination.

Indications of cleavage or decomposition reactions can be obtained by looking for changes in the chromatogram (for example the occurrence of foreign peaks or increase decrease in peak size) at various sample injector temperatures.

The two sample injection systems have been studied in interlaboratory tests, where the following observations were made.

The hot injection system includes all of the volatile constituents, solvents and cleavage products of the binders and additives. Cleavage products of the binders or additives which are identical to a solvent component can be separated by a cold injection system, since they elute later as a result of the programmed increase in injection block temperature (see Figure 2).

10 Procedure

10.1 Gas chromatographic conditions

10.1.1 General

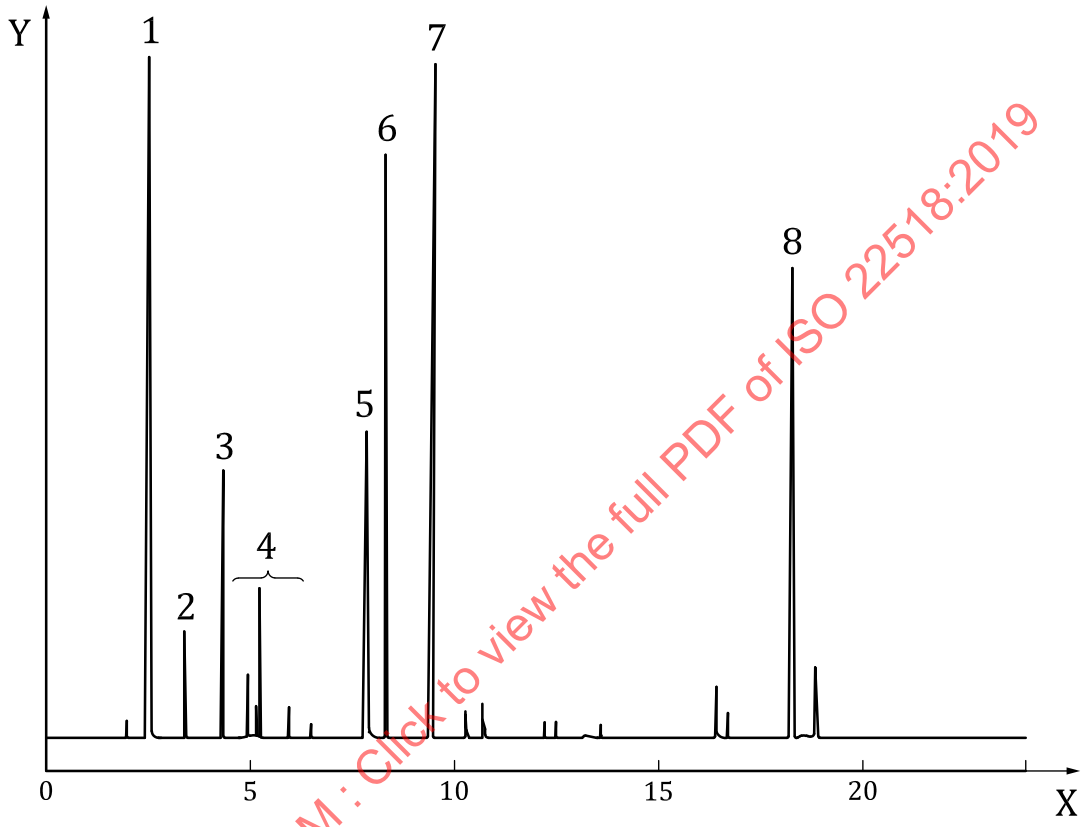
The gas chromatographic conditions used will depend on the product to be analyzed and shall be optimized each time using a known solvent mixture. 10.1.2 and 10.1.3 give examples of conditions for use with hot injection and cold injection, respectively.

10.1.2 Example of hot injection and gas chromatography of a water-thinnable coating material

Injector temperature:	250 °C	
Split ratio:	1: 40	
Injection volume:	0,5 µl, automatic injection	
Oven temperature program:	initial temperature:	70 °C
	isothermal holding time:	3 min
	heating rate:	10 K/min
	final temperature:	200 °C
	isothermal holding time:	25 min
Detector temperature:	260 °C	

Carrier gas:	helium, column inlet pressure 100 kPa
Separation column:	coated with poly(ethylene glycol), film thickness 0,2 µm, length 25 m, internal diameter 0,2 mm

A related gas chromatogram is shown in Figure 1.



Key

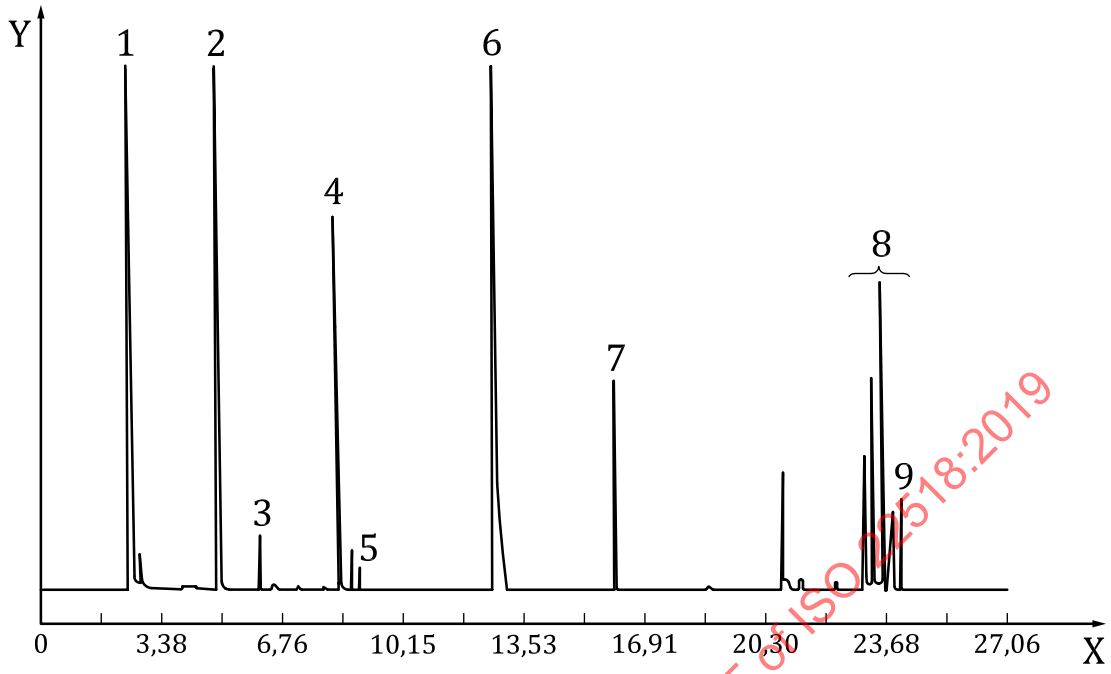
X retention time, in minutes
Y peak height
1 diluent (tetrahydrofuran)
2 methyl isobutyl ketone (MIBK)
3 2-methyl-1-propanol
4 ethylbenzene and xylene isomers
5 cleavage product from the binder
6 diethylene glycol dimethyl ester (internal standard)
7 ethylene glycol ether
8 1-phenoxypropan-2-ol1

Figure 1 — Gas chromatogram of a water-thinnable coating material A — Hot injection

10.1.3 Cold injection and gas chromatography of a water-thinnable coating material (example)

Temperature program of the		
cold injection system:	injection temperature:	30 °C
	heating rate:	10 K/min
	first holding temperature:	100 °C
	holding time:	10 s
	heating rate:	10 K/min
	second holding temperature:	260 °C
	holding time:	240 s
	split ratio:	1: 20
Injection volume:	0,2 µl	
Oven temperature program:	initial temperature:	50 °C
	isothermal holding time:	4 min
	heating rate:	8 K/min
	final temperature:	240 °C
	isothermal holding time:	10 min
Detector temperature:	280 °C	
Carrier gas:	hydrogen, column inlet pressure 150 kPa	
Separation column:	coated with polydimethylsioxane, film thickness 1,02 µm, length 50 m, internal diameter 0,32 mm	

A related gas chromatogram is shown in Figure 2.



Key

X retention time, in minutes
Y peak height
1 diluent (methanol)
2 2-methyl-1-propanol (internal standard)
3 1-methoxypropan-2-ol
4 1-ethoxypropan-2-ol
5 toluene
6 ethylene glycol butyl ether (solvent component and cleavage product component)
7 2-ethylhexanol
8 2,2,4-trimethyl-1,3-pentanediol isobutyrate
9 2,4,7,9-tetramethyl-5-decyne-4,7-diol

Figure 2 — Gas chromatogram of a water-thinnable coating material B — Cold injection

10.2 Injection volume

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

10.3 Calibration

Determine the correction factors by weighing out amounts of the solvents under test in the same order of magnitude as their respective content in the product and weigh out a similar amount of internal standard. Dilute the mixture with a suitable diluent (e.g. methanol or tetrahydrofuran) and separate it under the same conditions as used for the analytical sample. Calculate the correction factors. The mixture can be used to optimize instrumental parameters.

10.4 Sample preparation and analysis

Carefully homogenize the product and weigh out about 1 g to 3 g of it and an amount of internal standard in the same order of magnitude as the product under test into the sample vessel to the nearest

0,1 mg on an analytical balance. Dilute the sample in a ratio of about 1 : 3 with a suitable diluent such as methanol or tetrahydrofuran, seal the sample vessel and carefully homogenize the contents, for example by shaking or on a roller agitator.

Set the instrumental parameters optimized in advance and observed during calibration.

Inject 0,1 µl to 1,0 µl (see 10.2) of the sample into the gas chromatograph, record the chromatogram and identify the components contained in the product using a mass spectrometer, mass-selective detector or FT-IR spectrometer coupled to the gas chromatograph. If the components of products are known, they can be identified via their retention times or retention indices. Then, determine the components quantitatively.

11 Expression of results

Evaluate the results qualitatively and quantitatively. Calculate the amounts of the components contained in the product against the internal standard values using the correction factors determined.

12 Precision

12.1 General

The precision of the test method was determined in accordance with ISO 5725-1[1]. in a round robin test. Three coating materials were tested by 10 laboratories using the cold injection and hot injection method. Four solvents were analyzed.

The details of test matrix, solvent to be determined, concentration and injection method are shown in Table 1 and Table 2.

Table 1 — Test parameters for hot injection

Sample	Parameter	Methyl isobutyl ketone	Isobutanol	Butyl glycol	Phenoxy propanol
Dispersion 1	Number of laboratories	8	7	7	6
	general mean (%)	0,024 43	0,025 1	0,024 7	0,023 0
	reproducibility standard deviation	0,001 98	0,001 4	0,001 6	0,002 4
	reproducibility standard coefficient (%)	8,1	5,7	6,5	10,3
	repeatability standard deviation	0,001 80	0,001 3	0,000 7	0,001 5
	repeatability standard coefficient (%)	7,4	5,0	2,7	6,5
Dispersion 2	Number of laboratories	7	7	8	7
	general mean (%)	0,126 7	0,125 7	0,124 4	0,119 9
	reproducibility standard deviation	0,005 6	0,006 0	0,004 6	0,011 3
	reproducibility standard coefficient (%)	4,4	4,8	3,7	9,4
	repeatability standard deviation	0,005 0	0,006 0	0,001 0	0,003 4
	repeatability standard coefficient (%)	3,9	4,8	1,6	2,8
Kathodic deposition coating material	Number of laboratories	8	8	7	8
	general mean (%)	0,969	1,008	1,026	1,026
	reproducibility standard deviation	0,021	0,021	0,013	0,048
	reproducibility standard coefficient (%)	2,1	2,1	1,3	4,7
	repeatability standard deviation	0,015	0,012	0,005	0,021
	repeatability standard coefficient (%)	1,6	1,2	0,5	2,0