
**Paints and varnishes — Determination
of solvents in coating materials
containing organic solvents only —
Gas-chromatographic method**

*Peintures et vernis — Détermination des solvants dans les produits de
peinture contenant uniquement des solvants organiques — Méthode
par chromatographie en phase gazeuse*

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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

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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 16, *Chemical analysis*.

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 coating materials containing organic solvents only — Gas-chromatographic method

1 Scope

This document specifies a method for the gas-chromatographic determination of the qualitative and quantitative composition of solvents contained in a product. The method is applicable to coating materials containing solely organic solvents (generally called conventional coating materials) and binder solutions and non-aqueous dispersions containing solely organic solvents.

The method defined in this document is not applicable for determination of volatile organic compounds (VOC) and semi-volatile organic compounds (SVOC) content.

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

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*
<https://standards.iteh.ai/catalog/standards/sis/6c755e01-0d52-4b41-a4d5-bbc694177bf4/iso-23322-2021>

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 mass fraction.

5 Principle

The volatile fraction of the sample of product under test is separated by gas chromatography. Either a hot sample injection system, a cold sample injection system or a headspace 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 will not change it chemically.

6.1.2 Sample injection system

6.1.2.1 General

The method provides a choice between three sample injection systems:

- hot-injection system with sample splitter;
- cold-injection system with sample splitter;
- headspace injector.

6.1.2.2 Hot-injection system

The instrument shall have a variable-temperature injection block with sample splitter. The injection temperature shall be capable of being set to an accuracy of 1 K. Standard operating temperature shall be between 250 °C and 280 °C.

NOTE It is useful to use silanized glass wool to retain non-volatile constituents. The active sides of silanized glass wool can be a sink for organic compounds and significantly influence the recovery rate in the lower range of the method. The occurrence of adsorption is revealed by peak tailing, in particular with components of low volatility and/or high polarity.

6.1.2.3 Cold-injection system

The cold-injection system shall be provided with temperature programming for heating from ambient to 300 °C including a sample splitter for split operation.

NOTE It is useful to use silanized glass wool to retain non-volatile constituents. The active sides of silanized glass wool can be a sink for organic compounds and significantly influence the recovery rate in the lower range of the method. The occurrence of adsorption is revealed by peak tailing, in particular with components of low volatility and/or high polarity.

6.1.2.4 Headspace injection

It shall be possible to set the following values:

- controlled sample temperature: 150 °C;
- controlled transfer line and dispensing valve temperatures: 160 °C;
- temperature hold time: 4 min.

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

6.1.4.1 General

One of the following two detectors shall be used.

6.1.4.2 Mass spectrometer (MS) or other mass-selective detector (MSD)

To prevent condensation, the detector temperature shall be at least 10 K above the maximum oven temperature.

6.1.4.3 Flame ionization detector

The flame ionization detector (FID) is operated at temperatures between 230 °C and 300 °C. 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.

6.1.5 Capillary separation column

The column shall be made of glass or fused silica. Columns of sufficient length to resolve volatiles and of maximum internal diameter 0,32 mm, of a suitable polarity and with a suitable film thickness shall be used.

6.1.6 Analytical system performance criteria

The analytical system performance criteria shall be demonstrated. The resolution, R , of the peaks to be separated shall be at least 1,5.

For the compounds under investigation it has to be ensured that the sample concentration lies within the quantification range of the analytical system.

NOTE The limit of quantification can deviate for single compounds. If necessary, the compound specific limit of quantification can be determined for the considered single compound(s).

6.2 Injection syringe

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

6.3 Data processing

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

6.4 Sample vial

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

7 Reagents

7.1 General

[Table 1](#) shows a non-exhaustive list of an internal standards and extraction solvents.

Table 1 — List of reagents and their function

Reagent	CAS-No ^a	Abbreviation	Function
<i>n</i> -tetradecane	CAS-No 629-59-4	C14	internal standard
diethyladipate	CAS-No 141-28-6	DEA	internal standard
acetonitrile	CAS-No 75-05-8	ACN	extraction solvent
methanol	CAS-No 67-56-1	MEOH	extraction solvent
acetone	CAS-No 67-64-1	AC	extraction solvent
tetrahydrofuran	CAS-No 109-99-9	THF	extraction solvent

^a CAS-No: Chemical Abstracts Service Registry Number.

7.2 Internal standard

The internal standard should 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. The preferred internal standard is DEA.

NOTE If DEA is not suitable as internal standard, internal standards such as glycol ethers can be suitable.

7.3 Gases

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7.3.1 Carrier gas: Dry oxygen-free helium, nitrogen or hydrogen having a purity of at least 99,995 % (volume fraction).

7.3.2 Detector gases: Hydrogen having a purity of at least 99,995 % (volume fraction) and (synthetic) air-free of organic compounds.

7.3.3 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).

7.4 Calibration substances

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

7.5 Extraction solvent

For better handling of the direct injection, the sample may be diluted with suitable extraction solvents (e.g. acetone, CAS-No 67-64-1, methanol, CAS-No 67-56-1, acetonitrile, CAS-No 75-05-8 or tetrahydrofuran, CAS-No 109-99-9). The extraction solvents shall have a purity of at least 99 % (mass fraction) or be of known purity and shall not contain any substances which interfere with the determination by for example 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.

The suitability of a solvent or solvent mixture other than acetone, methanol and THF shall be checked by determining the recovery rates of analytes from the sample under investigation.

8 Sampling

Take a representative sample, as described in ISO 15528.

9 Choice of sample injection system

The choice between hot injection, cold injection and headspace injection depends on the type of the product under test. It will be 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 (e.g. the occurrence of foreign peaks or increase of peak size or peak broadening) at various sample injector temperatures.

The two sample injection systems hot injection and cold injection 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.

The headspace injector is primarily used for samples with a low content of organic solvents.

Headspace can only be used to analyse solvents with sufficient volatility at the controlled sample temperature.

10 Procedure ISO 23322:2021 <https://standards.iteh.ai/catalog/standards/sist/6c753e0f-0d32-4b41-a4d3-bbc694177bf4/iso-23322-2021>

10.1 Gas chromatographic conditions

The gas chromatographic conditions used will depend on the product to be analysed and shall be optimized each time using a known solvent mixture. Examples of suitable conditions are given in [Annex A](#).

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. Asymmetrical peaks (peak leading) will give an indication of overloading of the gas chromatographic system.

10.3 Calibration

10.3.1 General

Where suitable calibration compounds are commercially available, the relative response factor shall be determined using multi point calibration.

10.3.2 Preparation of calibration solutions

Weigh, into a sample vial (see [6.4](#)), to the nearest 0,1 mg, suitable amounts of the compounds determined in [10.5.1](#) which are of the same order of magnitude as their respective contents in the product under test.

Weigh a similar amount of the internal standard (see [7.2](#)) into the sample vial, dilute the mixture with extraction solvent (see [7.5](#)), and inject it under the same conditions as will be used for the test sample.

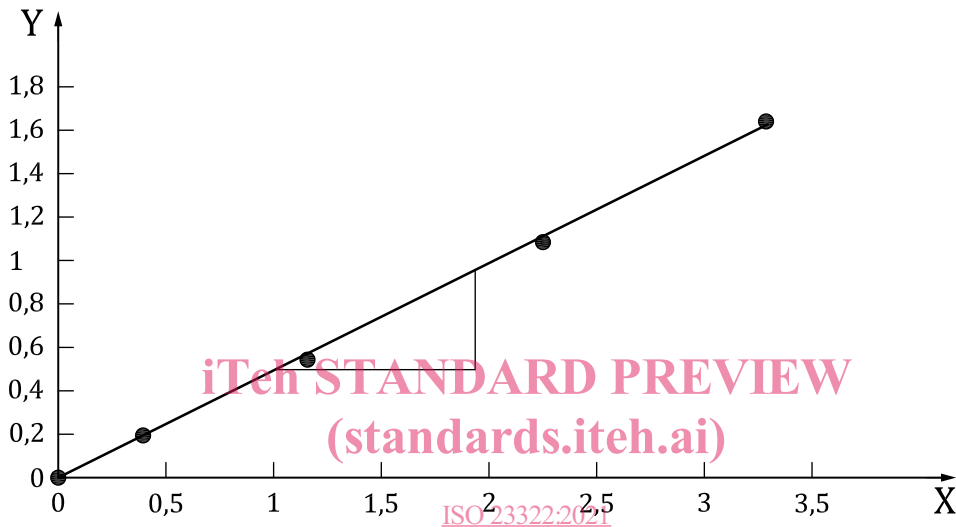
Repeat the procedure above two to seven times depending on the number of calibration points with different amounts, encompassing the respective contents in the product under test.

NOTE 1 Usually, a three- or five-point calibration is suitable.

NOTE 2 A one-point calibration is not suitable for the initial calibration of a compound because it does not allow to verify the linear relation between relative response and relative mass, see [Figure 1](#).

10.3.3 Analysis of the multi-point calibration

Inject suitable amounts of the calibration solutions into the gas chromatograph. Plot the mass of the compound under investigation relative to the internal standard mass versus the peak area of compound *i* divided by the peak area of the internal standard.



Key
 Y A_i/A_{is}
 X m_i/m_{is}

Figure 1 — Example of a multi-point calibration

Then carry out a linear regression to determine the slope of the curve, s_i . It represents the reciprocal of the compound specific relative response factor (CSRF), r_i . The function for linear regression, the relation between the slope of the curve and the CSRF and the calculation of the relative response factor, r_i , are given in the [Formulae \(1\), \(2\) and \(3\)](#).

$$\Delta \left(\frac{A_i}{A_{is}} \right) = s_i \cdot \Delta \left(\frac{m_i}{m_{is}} \right) \tag{1}$$

$$r_i = \frac{1}{s_i} \tag{2}$$

$$r_i = \frac{\Delta \left(\frac{m_i}{m_{is}} \right)}{\Delta \left(\frac{A_i}{A_{is}} \right)} \tag{3}$$

where