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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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Foreword

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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*

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
n-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

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 primary 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

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.

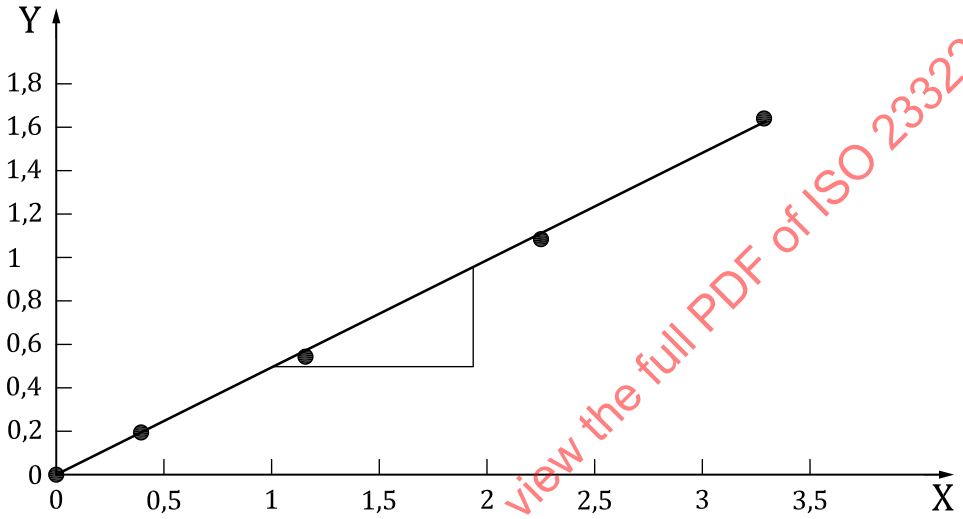
Repeat the procedure above two to seven times depending on the number of calibration points with different amounts, encompassing the respective contents in the product under test.

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

r_i is the CSRF (compound specific relative response factor);

s_i is the slope of the curve;

A_i is the peak area of compound *i*;

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

m_i is the mass, in grams, of compound *i* in the calibration solution;

m_{is} is the mass, in grams, of the internal standard in the calibration solution.

No offset other than statistical deviations should be observed. If a significant offset is recorded, results and the equipment should be checked and, if necessary, the analysis shall be repeated.

10.4 Quality assurance

Quality assurance may be used to check if the CSRF has changed and if a new calibration is necessary. An appropriate, e.g. mid-level, calibration solution can be used (see 10.3.2).

10.5 Sample preparation and analysis

Carefully homogenize the product.

10.5.1 Direct injection

Weigh a suitable amount of sample greater than 0,2 g (generally 1 g to 3 g is recommended) and an appropriate amount of the internal standard into a sample vial. Dilute the test sample with a suitable volume of extraction solvent (typically a dilution factor of 4 to 50 is applied, depending on the target compound concentration (see 10.3.2), seal the vial and homogenize the contents. When necessary, use methods such as stirring, vortexing or ultrasonic mixing to support extraction. If particles do not readily settle, phase cleaning can be obtained by centrifugation or filtration.

The internal standard concentration should be chosen at such level that detector signal precision and recovery from the pre-treated sample are optimal.

Repeat the procedure and perform at least a duplicate analysis.

10.5.2 Head space injection

Sample preparation involves diluting the sample and preparing the test samples. If appropriate, standard additions can be used for quantification

NOTE A possible standard addition method is described in detail in ISO 17895.

Carry out the sample preparation quickly since the original sample diluted with citrate buffer is prone to serum formation and losses may occur as the result of volatilization of individual compounds.

For dilution of original sample, weigh 10 g of the original sample and 10 g of citrate buffer to the nearest 0,1 g into a 20 ml septum vial, seal and mix.

10.5.3 Preparation of test samples for analysis without multiple standard additions

Vigorously shake the sealed septum vial containing the diluted sample (prepared as in 10.5.2), then immediately remove any excess vapour by piercing the septum with a 2 ml disposable syringe. For the analysis, weigh aliquots of (15 ± 3) mg to the nearest 0,1 mg into each of three vials and seal the latter immediately.

NOTE Higher initial test sample masses result in errors in the result due to the increase in pressure.

10.5.4 Data acquisition for sample measurement

Set the instrumental parameters as optimized during calibration.

Inject 0,1 µl to 1 µl of the test sample into the gas chromatograph or inject 500 µl to 1 000 µl for headspace injection, respectively. Record the chromatogram using a mass-selective detector or FID detector coupled to the gas chromatograph. Determine the peak areas for each compound.

If the components of products are known, they can be identified via retention times or retention indices. Otherwise use a mass selective detector for identification. Then determine the components quantitatively.

11 Quantitative determination of compound content with respect to CSRF

All solvent peaks shall be quantified with an FID detector or mass detector under the same analytical conditions using the CSRF.

Determine the mass fraction, in %, of all compounds of the product using Formula (4):

$$f_i = \frac{r_i \times A_i \times m_{is}}{m_s \times A_{is}} \times 100 \quad (4)$$

where

f_i is the mass fraction of compound i in % of the product;

r_i is the CSRF for compound i;

A_i is the peak area of compound i;

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

m_{is} is the mass, in grams, of internal standard in the test sample;

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

12 Expression of results

Evaluate the results qualitatively and quantitatively.

If two results from duplicate determination differ by more than the repeatability limit r from each other, repeat the procedure. State the amounts of the components contained in the product to 100 % as stated in.

Calculate the mean of two valid results (replicates). For values greater than 1 % (mass fraction), report to the nearest 0,1 %; for values less than or equal to 1 % (mass fraction) and larger than or equal to 0,1 % (mass fraction), report the result to the nearest 0,01 %. For values < 0,1 % (mass fraction) report to the nearest 0,005 % (mass fraction).

13 Precision

13.1 Repeatability

The repeatability limit r is the value below which the absolute difference between two single test results, each the mean of duplicates, can be expected to lie with a 95 % probability when this method is used under repeatability conditions, i.e. when the test results are obtained on identical material by one operator in one laboratory within a short interval of time.

For this test method, the repeatability is 3 % (related to the arithmetic mean value).

13.2 Reproducibility

The reproducibility limit *R* is the value below which the absolute difference between two single test results, each the mean of duplicates, can be expected to lie with a 95 % probability when this method is used under reproducibility conditions, i.e. when the test results are obtained on identical material by operators in different laboratories.

For this test method, the reproducibility is 10 % (related to the arithmetic mean value).

14 Test report

The test report shall contain at least the following information:

a) all details necessary to identify the product tested;

b) a reference to this document, i.e. ISO 23322:2021;

c) all agreed details, such as sample preparation, sample injection system and gas chromatographic conditions;

d) the result of the test, as specified in Clause 12;

e) any deviation from the test method specified;

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

g) the date of the test.

Annex A
(informative)

Examples for GC method conditions

A.1 General

The gas chromatographic conditions shall be adjusted to the instrumental circumstances. A.1 and A.2 give respective examples of conditions for use with hot injection and cold injection. A.3 and A.4 give two examples for headspace injection (from ISO 17895:2005, 8.3.2).

A.2 Example 1: Gas chromatographic conditions for use with hot injection

Injector temperature:	250 °C	
Split ratio:	1 : 100	
Injection volume:	0,2 µl	
Oven temperature program:	Initial temperature:	40 °C
	Heating rate:	3 K/min
	Final temperature:	175 °C
Detector temperature:	260 °C	
Carrier gas:	Helium, column inlet pressure 170 kPa	
Separation column:	Coated with poly(ethylene glycol), film thickness 0,25 µm, length 50 m, internal diameter 0,2 mm	

A.3 Example 2: Gas chromatographic conditions for use with cold injection

Temperature program of the cold injection system:	Injection temperature:	40 °C
	Heating rate:	10 K/s
	First holding temperature:	100 °C
	Holding time:	10 s
	Heating rate:	10 K/s
	Second holding temperature:	250 °C
	Holding time:	200 s