
**Paints and varnishes — Determination of
volatile organic compound (VOC)
content —**

**Part 2:
Gas-chromatographic method**

iTeh STANDARD PREVIEW

*Peintures et vernis — Détermination de la teneur en composés
organiques volatils (COV)*
(standard iTeh.ai)

Partie 2: Méthode par chromatographie en phase gazeuse

ISO 11890-2:2006

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 11890-2 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*.

This second edition cancels and replaces the first edition (ISO 11890-2:2000), which has been technically revised. The main changes are:

- the method has been modified to allow the determination of the VOC content when the term refers to compounds with a well-defined boiling point;
- the calculation of the VOC content of a product "ready for use" less water and less exempt compounds (see 10.5) has been modified to make it clear that only those components that are not exempt compounds are considered.

ISO 11890 consists of the following parts, under the general title *Paints and varnishes — Determination of volatile organic compound (VOC) content*:

- *Part 1: Difference method*
- *Part 2: Gas-chromatographic method*

Paints and varnishes — Determination of volatile organic compound (VOC) content —

Part 2: Gas-chromatographic method

1 Scope

This part of ISO 11890 is one of a series of standards dealing with the sampling and testing of paints, varnishes and related products.

It specifies a method for the determination of the volatile organic compound (VOC) content of paints, varnishes and their raw materials. This part is preferred if the expected VOC content is greater than 0,1 % by mass and less than about 15 % by mass. When the VOC content is greater than about 15 % by mass, the less complicated method given in ISO 11890-1 may be used.

This method assumes that the volatile matter is either water or organic. However, other volatile inorganic compounds can be present and might need to be quantified by another suitable method and allowed for in the calculations.

2 Normative references

[ISO 11890-2:2006](https://standards.iteh.ai/catalog/standards/sist/8ae87a42-12c8-486f-8184-9a027948e865/iso-11890-2-2006)

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The following referenced documents are indispensable for the application 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 samples for testing*

ISO 2811-1, *Paints and varnishes — Determination of density — Part 1: Pycnometer method*

ISO 2811-2, *Paints and varnishes — Determination of density — Part 2: Immersed body (plummet) method*

ISO 2811-3, *Paints and varnishes — Determination of density — Part 3: Oscillation method*

ISO 2811-4, *Paints and varnishes — Determination of density — Part 4: Pressure cup method*

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

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1 volatile organic compound VOC

any organic liquid and/or solid that evaporates spontaneously at the prevailing temperature and pressure of the atmosphere with which it is in contact

NOTE 1 As to current usage of the term VOC in the field of coating materials, see volatile organic compound content (VOC content).

NOTE 2 Under U.S. government legislation, the term VOC is restricted solely to those compounds that are photochemically active in the atmosphere (see ASTM D 3960). Any other compound is then defined as being an exempt compound.

[ISO 4618:2006]

NOTE 3 Under European legislation, EU Directive 2004/42/EC, the term VOC refers to volatile organic compounds with boiling points up to 250 °C, measured at a standard pressure of 101,3 kPa.

3.2 volatile organic compound content VOC content

mass of the volatile organic compounds present in a coating material, as determined under specified conditions

NOTE 1 The properties and the amounts of the compounds to be taken into account will depend on the field of application of the coating material. For each field of application, the limiting values and the methods of determination or calculation are stipulated by regulations or by agreement.

[ISO 4618:2006]

NOTE 2 If the term VOC refers to compounds with a defined maximum boiling point (see Note 3 to 3.1), the compounds considered to be part of the VOC content are those with boiling points below that limit and compounds with higher boiling points are considered to be non-volatile organic compounds.

3.3 exempt compound

organic compound that does not participate in atmospheric photochemical reactions

NOTE See Notes 2 and 3 to 3.1.

3.4 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

4 Principle

After preparation of the sample, the VOCs are separated by a gas-chromatographic technique. Either a hot or a cold sample injection system is used, depending on the sample type. Hot injection is the preferred method. After the compounds have been identified, they are quantified from the peak areas using an internal standard. Depending on the equipment used, it may also be possible to determine the water content by this method. A calculation is then performed to give the VOC content of the sample.

5 Required supplementary information

For any particular application, the test method specified in this part of ISO 11890 needs to be completed by supplementary information. The items of supplementary information are given in Annex A.

6 Apparatus

6.1 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.

6.2 Sample injection system

6.2.1 General

Use one of the two types specified in 6.2.2 and 6.2.3.

6.2.2 Hot-injection system with sample splitter (preferred 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 non-volatile constituents, and 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 (i.e. adsorption of compounds). The occurrence of adsorption is revealed by peak tailing, in particular with components of low volatility.

6.2.3 Cold-injection system with sample splitter

The cold-injection system shall be provided with temperature programming for heating from ambient to 300 °C and shall have a sample splitter inlet which is made of an inert material such as glass. The sample splitter shall be provided with silanized glass wool packing and shall be maintained as specified in 6.2.2. The split ratio shall be adjustable and capable of being monitored.

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

6.2.4 Selection of sample injection system

The choice between hot-injection and cold-injection will depend on the type of 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 may be obtained by looking for changes in the chromatogram (for example the occurrence of foreign peaks or an increase or decrease in peak size) at various sample injector temperatures.

The hot-injection system covers all of the volatile constituents, compounds and cleavage products of the binders and additives. Cleavage products of the binders or additives which are identical to a constituent of the product can be separated by a cold-injection system, since they elute later as a result of the programmed increase in injection block temperature.

6.3 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 6.5).

6.4 Detector

Any of the following three detectors may be used, as well as other detectors suitable for specific types of compound:

6.4.1 Flame ionization detector (FID), capable of being operated at temperatures up to 300 °C. To prevent condensation, the detector temperature shall be at least 10 °C 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.

6.4.2 Suitably calibrated and tuned mass spectrometer or other mass-selective detector.

6.4.3 Suitably calibrated Fourier-transform infrared spectrometer (FT-IR spectrometer).

6.5 Capillary 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, coated with unmodified or phenyl-modified poly(dimethylsiloxane) or poly(ethylene glycol) at a suitable film thickness, have been shown to give good peak separation. The stationary phase and column length shall be chosen to suit the particular separation (see examples in Annex B).

A suitable combination of column, temperature programme and marker compound shall be chosen such that compounds in the sample which are defined as VOCs by virtue of their boiling point (see Note 3 to 3.1) elute before the boiling-point marker compound (see 7.4) and those which are not VOCs elute after the marker compound. When the boiling-point limit is set at 250 °C and a polar stationary phase is used, the marker compound given in 7.4, with a DB-1301™ column, or equivalent, at least 60 m in length and with an internal diameter of 0,32 mm, and with a film thickness of approximately 1 µm, is recommended.

6.6 Qualitative-analysis equipment

If the separated components are to be identified by a mass-selective detector or FT-IR spectrometer, the instrument shall be coupled to the gas chromatograph and operated in accordance with the manufacturer's instructions.

6.7 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.

6.8 Chart recorder

Compensating chart recorders are suitable for plotting the gas chromatogram.

6.9 Integrator

An electronic data-processing system (integrator or computer) shall be used to measure the peak areas. The integration parameters used in calibration and analysis shall be identical.

6.10 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 polytetrafluoroethylene).

6.11 Gas filters

Filters shall be installed in the gas chromatograph connection pipes to adsorb residual impurities in the gases (see 6.12).

6.12 Gases

6.12.1 Carrier gas: dry, oxygen-free helium, nitrogen or hydrogen, having a purity of at least 99,996 % by volume.

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

6.12.3 Auxiliary gas: nitrogen or helium of the same quality as the carrier gas.

7 Reagents

7.1 Internal standard

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. Compounds such as isobutanol and diethylene glycol dimethyl ether have been found suitable.

7.2 Calibration compounds

The compounds used for calibration shall have a purity of at least a 99 % by mass or shall be of known purity.

7.3 Dilution solvent

Use an organic solvent suitable for diluting the sample. It shall have a purity of at least 99 % by mass 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.

NOTE Solvents such as methanol and tetrahydrofuran have been found suitable.

7.4 Marker compound

If the term VOC is being used for compounds whose boiling points are below a defined maximum limit (see Note 3 to 3.1), a marker compound of known purity and with a boiling point within ± 3 °C of the defined maximum limit shall be used.

EXAMPLE If the defined maximum boiling point is 250 °C, tetradecane, with a boiling point of 252,6 °C, could be used as the marker compound for non-polar systems and diethyl adipate, with a boiling point of 251 °C, as the marker compound for polar systems.

8 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.

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

9 Procedure

9.1 Density

If required by the calculation (see 10.3 to 10.5), determine the density of the sample using the part of ISO 2811 which will give the best precision for the type of sample concerned. Determine the density at 23 °C.

9.2 Water content

If required by the calculation (see 10.4 and 10.5), determine the water content, as a percentage by mass, by the method given in ISO 760, selecting the reagents so that there will be no interference from the compounds contained in the sample. If the compounds are not known, then determine them qualitatively (see 9.4).

NOTE 1 Typical compounds likely to cause interference are ketones and aldehydes. Reagent manufacturers normally publish literature for guidance on correct reagent selection.

NOTE 2 If the product to be tested is well characterized and known not to contain water, it may not be necessary to determine the water content, which can be assumed to be zero.

9.3 Gas-chromatographic conditions ISO 11890-2:2006

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9.3.1 The gas-chromatographic conditions used will depend on the product to be analysed and shall be optimized each time using a known calibration mixture. See Annex B for examples of conditions for use with hot-injection and cold-injection systems.

9.3.2 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.

9.4 Qualitative analysis of product

If the organic compounds in the product are not known, then determine them qualitatively. A gas chromatograph coupled to a mass-selective detector or FT-IR spectrometer (6.6), with the chromatograph programmed to the same settings as will be used in 9.3, is the preferred method.

9.5 Calibration

9.5.1 Where suitable compounds are commercially available, the response factor shall be determined using the following technique:

9.5.1.1 Weigh, into a sample vial (6.10), to the nearest 0,1 mg, amounts of the compounds determined in 9.4 which are of the same order of magnitude as their respective contents in the product under test.

Weigh out a similar amount of the internal standard (7.1) into the sample vial, dilute the mixture with the dilution solvent (7.3), and inject it under the same conditions as will be used for the test sample.

9.5.1.2 Optimize the instrumental parameters as indicated in 9.3.

9.5.1.3 Again inject a suitable amount of the calibration mixture into the gas chromatograph. Calculate the response factors for each of the compounds using Equation (1):

$$r_i = \frac{m_{Ci} \times A_{iS}}{m_{iS} \times A_{Ci}} \quad (1)$$

where

r_i is the response factor for compound i ;

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

m_{Ci} is the mass, in grams, of compound i in the calibration mixture;

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

A_{Ci} is the peak area of compound i .

9.5.2 Where unidentified peaks are found or where suitable compounds are not commercially available, a response factor of 1,0 shall be assumed.

9.6 Sample preparation

Weigh, to the nearest 0,1 mg, approximately 1 g to 3 g of the sample and an amount of the internal standard which is of the same order of magnitude as the analytes into a sample vial. Dilute the test sample with a suitable volume of dilution solvent, seal the vial and homogenize the contents.

NOTE Pigmented or otherwise difficult samples may be cleaned up by centrifuging.

9.7 Quantitative determination of compound content

9.7.1 Set the instrumental parameters as optimized during calibration.

9.7.2 If the term VOC is being used for compounds whose boiling points are below a given maximum limit (see Note 3 to 3.1), determine the retention time of the marker compound by a separate GC analysis. This retention time defines the integration end-point for the VOC determination in the chromatogram. A column which gives elution times that are related to the boiling point shall be used.

9.7.3 Inject 0,1 μ l to 1 μ l of the test sample into the gas chromatograph and record the chromatogram. Determine the peak areas for each compound or, if the term VOC is being used for compounds whose boiling points are below a given maximum limit (see Note 3 to 3.1), determine the peak areas for all compounds with retention times lower than that of the marker compound. Determine the mass of all such compounds present in 1 g of the product using Equation (2):

$$m_i = \frac{r_i \times A_i \times m_{iS}}{m_S \times A_{iS}} \quad (2)$$

where

m_i is the mass, in grams, of compound i in 1 g of the product;

r_i is the response factor for compound i (see 9.5.1.3);

A_i is the peak area of compound i ;

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