INTERNATIONAL STANDARD

ISO 11890-2

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

Part 2:
Gas-chromatographic method

Peintures et vernis — Détermination de la teneur en composés organiques volatils (COV) —

Partie 2: Méthode par chromatographie en phase gazeuse

Reference number
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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 third edition cancels and replaces the second edition (ISO 11890-2:2006), of which it constitutes a minor revision to correct the numerator of the fraction in Equation (6) in 10.5.

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

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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 2811-1, *Paints and varnishes — Determination of density — Part 1: Pyknometer 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 to entry: As to current usage of the term VOC in the field of coating materials, see volatile organic compound content (VOC content).

Note 2 to entry: Under US government legislation, the term VOC is restricted solely to those compounds that are photochemically active in the atmosphere (see ASTM D3960). Any other compound is then defined as being an exempt compound.

Note 3 to entry: 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.

[SOURCE: ISO 4618:2006, modified — Note 3 to entry has been added.]

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 to entry: 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.

Note 2 to entry: 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.

[SOURCE: ISO 4618:2006, modified — Note 2 to entry has been added.]

3.3
exempt compound
organic compound that does not participate in atmospheric photochemical reactions

Note 1 to entry: See Note 2 to entry and Note 3 to entry in 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 might 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 can 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[1], 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 poly(tetra fluoro ethylene)].

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.

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[1] DB-1301 is the trademark of a product supplied by Agilent Technologies J&W. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

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, water 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 might not be necessary to determine the water content, which may be assumed to be zero.

9.3 Gas-chromatographic conditions

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 a similar amount of the internal standard (7.1) into the sample vial, dilute the mixture with 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):

$$r_i = \frac{m_{ci} \times A_{is}}{m_{is} \times A_{ci}} \qquad (1)$$

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 µl to 1 µl 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):

$$m_i = \frac{r_i \times A_i \times m_{\text{is}}}{m_{\text{s}} \times A_{\text{is}}} \qquad (2)$$

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;

m_{is} is the mass, in grams, of internal standard in the test sample (see 9.6);

m_{s} is the mass, in grams, of the test sample (see 9.6).

NOTE Some solvents, such as naphtha, will elute as a series of peaks. With most recording integrators, the total area may be summed and treated as one peak, provided no other compounds coelute over this interval. If the integrator does not have this capability, then the total area will have to be summed manually. The equation above can then be used to determine the amount of solvent in the test sample.

9.7.4 Repeat the procedure.

10 Calculation

10.1 General

Calculate the VOC content by the method specified in the referring specification. If no particular method is specified, calculate the VOC content by method 1.

Method 1 is the preferred calculation method as the precision is better since it does not involve the determination of density (which introduces the potential for additional errors).

10.2 Method 1: VOC content, as a percentage by mass, of the product “ready for use”

$$\text{VOC} = \sum_{i=1}^{i=n} m_i \times 100 \qquad (3)$$

where

VOC is the VOC content, as a percentage by mass, of the product “ready for use”;

m_i is the mass, in grams, of compound *i* in 1 g of the test sample (see 9.7.3);

100 is a conversion factor to convert from mass (grams per gram) to a percentage.

10.3 Method 2: VOC content, in grams per litre, of the product “ready for use”

$$\mathrm{VOC}=\sum_{i=1}^{i=n} m_i \times \rho_\mathrm{s} \times 1\,000 \qquad (4)$$

where

VOC	is the VOC content, in grams per litre, of the product “ready for use”;
m_i	is the mass, in grams, of compound *i* in 1 g of the test sample (see 9.7.3);
ρ_s	is the density, in grams per millilitre, of the test sample at 23 °C (see 9.1);
1 000	is a conversion factor to convert from mass (grams per gram) to grams per litre.

10.4 Method 3: VOC content, in grams per litre, of the product “ready for use” less water

$$\mathrm{VOC}_\mathrm{lw}=\left(\frac{\sum_{i=1}^{i=n} m_i}{1-\rho_\mathrm{s}\times\frac{m_\mathrm{w}}{\rho_\mathrm{w}}}\right)\times \rho_\mathrm{s} \times 1\,000 \qquad (5)$$

where

VOC_lw	is the VOC content, in grams per litre, of the product “ready for use” less water;
m_i	is the mass, in grams, of compound *i* in 1 g of the test sample (see 9.7.3);
m_w	is the mass, in grams, of water in 1 g of the test sample (see 9.2);
ρ_s	is the density, in grams per millilitre, of the test sample at 23° C (see 9.1);
ρ_w	is the density, in grams per millilitre, of water at 23 °C (= 0,997 537 g/ml);
1 000	is a conversion factor.

10.5 Method 4: VOC content, in grams per litre, of the product “ready for use” less water and less exempt compounds (only required if national legislation applies)

$$\mathrm{VOC}_{\mathrm{lwe}} = \left(\frac{\sum\limits_{i=1}^{i=n} m_i}{1 - \rho_{\mathrm{s}} \times \dfrac{m_{\mathrm{w}}}{\rho_{\mathrm{w}}} - \rho_{\mathrm{s}} \times \sum\limits_{\mathrm{eci}=1}^{\mathrm{eci}=n} \dfrac{m_{\mathrm{eci}}}{\rho_{\mathrm{eci}}}} \right) \times \rho_{\mathrm{s}} \times 1\,000 \qquad (6)$$

where

$\mathrm{VOC}_{\mathrm{lwe}}$	is the VOC content, in grams per litre, of the product “ready for use” less water and less exempt compounds;
m_i	is the mass, in grams, of compound *i* in 1 g of the test sample without exempt compound (see 9.7.3);
m_{eci}	is the mass, in grams, of exempt compound *i* in 1 g of the test sample;
m_{w}	is the mass, in grams, of water in 1 g of the test sample (see 9.2);
ρ_{s}	is the density, in grams per millilitre, of the test sample at 23 °C (see 9.1);
ρ_{w}	is the density, in grams per millilitre, of water at 23 °C (= 0,997 537 g/ml);
ρ_{eci}	is the density, in grams per millilitre, of exempt compound *i*;
1 000	is a conversion factor.

11 Expression of results

If the two results (duplicates) differ by more than the maximum value indicated in 12.2, repeat the procedure.

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

12 Precision

12.1 General

The precision of the test method was determined by interlaboratory testing in accordance with ISO 5725-1 and ISO 5725-2. Four different materials were tested by five to seven laboratories. Some of the results were not considered when calculating the precision because they were not in the scope of the test method (see Footnote “a” to Table 1). Their VOC content was above 15 % by mass but they were tested for a better comparison with the precision of ISO 11890-1.

12.2 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 five repeated determinations made using this test method, expressed as the repeatability coefficient of variation, lies between 1 % and 8 %.

12.3 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, may be expected to lie.

The reproducibilty for this test method, expressed as the reproducibility coefficient of variation, lies between 2 % and 11 %.

Table 1 — Results of interlaboratory testing

Parameter	Dispersion	Cathodic electro-deposition paint	Water-based paint	Two-component varnish [a]
Number of laboratories	5	7	5	6
Number of repeated determinations	5	5	5	5
Mean VOC value, % by mass	0,36	11,68	11,83	43,36
Reproducibility standard deviation	0,04	0,24	1,22	4,73
Reproducibility coefficient of variation	10,4	2,0	10,3	10,9
Repeatability standard deviation	0,01	0,17	0,88	0,64
Repeatability coefficient of variation	2,6	1,5	7,4	1,5

[a] Not considered for the precision because the mean VOC value is above 15 % by mass.

13 Test report

The test report shall contain at least the following information:

a) a reference to this part of ISO 11890 (ISO 11890-2);

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

c) the items of supplementary information referred to in Annex A;

d) a reference to the international or national standard, product specification or other document supplying the information referred to in c) above;

e) the results of the test, as indicated in Clause 10, and the method of calculation used (10.2, 10.3, 10.4 or 10.5);

f) any deviation from the test method specified;

g) the date of the test.

Annex A
(normative)

Required supplementary information

The items of supplementary information listed in this annex shall be supplied as appropriate to enable the method to be carried out.

The information required should preferably be agreed between the interested parties and may be derived, in part or totally, from an international or national standard or other document related to the product under test.

a) The organic compound(s) to be determined (see Clause 9).

b) The experimental conditions to be used (see Clause 9).

c) The boiling-point marker compound used (see 7.4).

d) Which of the organic compounds in a) are exempt compounds.

e) The method of calculation to be used (see Clause 10).

Annex B
(informative)

Examples of gas-chromatographic conditions

B.1 Hot injection of a water-thinnable product

Injector temperature:	250 °C
Split ratio:	1:40
Injection volume:	0,5 µl, automatic injection
Oven temperature programme:	initial temperature: 100 °C
	isothermal holding time: 1 min
	heating rate: 20 °C/min
	final temperature: 260 °C
	isothermal holding time: 21 min
Detector temperature:	260 °C
Carrier gas:	helium
	column inlet pressure: 124 kPa (18 psi)
	linear flow rate through column: 27,3 cm/s at 100 °C oven temperature
Column:	length: 60 m
(A DB-1301™ column 1) has been found suitable)	internal diameter: 0,32 mm
	coated with 6 % cyanopropyl-phenyl/94 % methylpolysiloxane
	film thickness: 1 µm