International
Standard

ISO 17895

Second edition
2024-08

Paints and varnishes — Determination of volatile organic compound (VOC) — Gas-chromatographic method with headspace injection for VOC determination

Peintures et vernis — Détermination de la teneur en composés organiques volatils (COV) — Méthode par chromatographie en phase gazeuse avec injection dans l'espace de tête pour la détermination des COV

Reference number
ISO 17895:2024(en)

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Published in Switzerland

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Foreword

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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 document 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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This document was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 16, *Chemical analysis,* in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 139, *Paints and varnishes,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 17895:2005), which has been technically revised.

The main changes are as follows:

- the document has been technically revised;
- used methods have been further specified;
- normative references have been updated.

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 volatile organic compound (VOC) — Gas-chromatographic method with headspace injection for VOC determination

WARNING — The use of this document can involve hazardous materials, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of users of this document to take appropriate measures to ensure the safety and health of personnel prior to the application of the document, and to determine the applicability of any other restrictions for this purpose.

1 Scope

This document specifies the sampling and testing of low volatile organic compound (VOC) coating materials and their raw materials. In particular, this document specifies a gas-chromatographic method to quantitatively determine the VOC content (i.e. the content of organic compounds with boiling points up to 250 °C) under standard conditions (101,325 kPa). It is applicable to VOC contents between 0,01 % and 0,1 % by mass.

This document does not apply to the determination of the semi-volatile organic compounds (SVOC) content, which is covered in ISO 11890-2.

This document does not apply to volatile organic and volatile inorganic compounds that cannot be determined by gas chromatography.

The procedure for identifying the appropriate method for the determination of VOC content and the SVOC content of coating materials and their raw materials is described in ISO/TR 5601.

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 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 3696, *Water for analytical laboratory use — Specification and test methods*

3 Terms and definitions

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

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at https://www.electropedia.org/

3.1
volatile organic compound
VOC

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* (3.9), see *volatile organic compound content* (3.3).

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.

[SOURCE: ISO 4618:2023, 3.266, modified — Note 3 to entry has been removed.]

3.2
semi-volatile organic compound
SVOC

organic liquid and/or solid that evaporates spontaneously but slower in comparison to VOC at the prevailing temperature and pressure of the atmosphere with which it is in contact

Note 1 to entry: Regarding current usage of the term SVOC in the field of *coating materials* (3.9), see *semi-volatile organic compound content* (3.4).

[SOURCE: ISO 4618:2023, 3.227]

3.3
volatile organic compound content
VOC content

mass of the *volatile organic compounds* (3.1) present in a *coating material* (3.9), as determined under specified conditions

Note 1 to entry: The properties and the amounts of the compounds to be taken into account 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, the compounds considered to be part of the VOC content are those with boiling points below and including that limit, and compounds with higher boiling points are considered to be *semi-volatile* (3.2) or non-volatile organic compounds.

[SOURCE: ISO 4618:2023, 3.267 modified — Note 2 to entry has been added.]

3.4
semi-volatile organic compound content
SVOC content

mass of the *semi-volatile organic compounds (SVOC)* (3.2) present in a *coating material* (3.9), as determined under specified conditions

Note 1 to entry: The properties and the amounts of the compounds to be taken into account 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 SVOC refers to compounds with a defined maximum boiling point and minimum boiling point, the compounds considered to be part of the SVOC content are as followed:

— compounds above the lower limit value (lower limit value not included) and;

— compounds lower or equal to the upper limit (upper limit included).

Compounds with boiling points higher than the upper limit for SVOC are considered to be non-volatile organic compounds.

[SOURCE: ISO 4618:2023, 3.228, modified — Note 2 to entry has been modified.]

3.5
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

Note 1 to entry: In context of this VOC emission standard, only waterbased thinners will be of relevance.

3.6
surrogate standard
compound of known purity which is used to quantify unidentified *volatile organic compounds* (3.1)

3.7
marker compound
compound which is used to differentiate between *volatile organic compounds (VOC)* (3.1) and *semi-volatile organic compounds (SVOC)* (3.2), or SVOC and non-volatile organic compound if the differentiation is made on the basis of *retention time* (3.8)

3.8
retention time
t_R
time elapsed from injection of the sample component to the recording of the peak maximum

3.9
coating material
product, in liquid, paste or powder form, that, when applied to a substrate, forms a layer possessing protective, decorative and/or other specific properties

[SOURCE: ISO 4618:2023, 3.48]

4 Principle

The volatile organic compounds (VOC) in a very small amount of a thinned sample are fully evaporated in a headspace injector and then determined by gas-chromatographic analysis, as follows.

A few microlitres of the sample diluted with a buffer solution are heated to 150 °C in a septum-sealed vial. When fully evaporated, some of the vapour phase is transferred to a non-polar capillary column. The peak areas of all the components with retention times less than that of the marker compound (tetradecane, boiling point 250 °C) are integrated. Standard additions of a surrogate standard are employed at four concentration levels to determine the VOC content. The result is based on the response factor of the surrogate standard.

For a series of samples with the same matrix, quantification via an external standard can be applied.

NOTE The determination of individual components in the sample, or of standards prepared separately from coating materials or their raw materials which are as free of VOCs as possible, can be used to validate the analytical system.

5 Required information

For any particular application, the information required should preferably be agreed between the interested parties and may be derived, partially or totally, from an international or national standard or other document related to the product under test.

The method of calculation used shall be indicated (see Clause 10).

6 Apparatus

The usual laboratory apparatus and, in particular, the following shall be used.

6.1 Gas chromatograph (GC)

6.1.1 General

All instrumental parts which come into contact with the test sample shall be made of a material (e.g. glass), which is resistant to the sample and does not change it chemically.

6.1.2 Headspace injector, preferably with an automatic sample changer.

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 °C. The final temperature of the temperature programme shall not exceed the maximum operating temperature of the capillary column (see 6.1.5).

6.1.4 Detector

A flame ionization detector (FID) shall be used, for quantification of VOC compounds operated at temperatures between 230 °C and 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.

6.1.5 Capillary column

A non-polar fused-silica capillary column shall be used, with a stationary phase consisting of 95 % to 100 % dimethylsilicone and 5 % to 0 % of phenylsilicone chemically bound to the column.

NOTE Capillary columns having a length of 30 m and an internal diameter of 0,32 mm coated with 95 % dimethylsilicone and 5 % phenylsilicone (film thickness approximately 1 µm) were found to be suitable in an interlaboratory trial.

6.1.6 Gas filters

Filters shall be installed in the gas chromatograph connection pipes to adsorb residual impurities in the gases (see 6.1.7).

6.1.7 Gases

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

6.1.7.2 Detector gases, hydrogen having a purity of at least 99,999 % by volume and purified or synthetic air, free of organic compounds.

6.1.8 Data processing

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

6.2 Microlitre syringe, having a capacity of 50 µl.

6.3 Disposable plastic syringe, having a capacity of 2 ml.

6.4 Septum-sealable vials, having a capacity of about 20 ml, with a butyl or silicone rubber septum coated with polytetrafluoroethylene (PTFE). Since the test conditions specified in this document result in fairly high pressures in the vials, care shall be taken to ensure that they are tightly sealed.

6.5 Volumetric flask, having a capacity of 1 l.

6.6 Analytical balance, accurate to 0,1 mg.

7 Reagents

7.1 Demineralized water, of grade 1 in accordance with ISO 3696.

Demineralized water tends to cause microbial contamination. Demineralized water with low microbial contamination [colony forming units (CFU) < 100] should be used, or it should be tested that a microbial contamination of the demineralized water has no influence on the measurement result. Formaldehyde as a preservative can potentially react with microorganisms.

7.2 Surrogate standard

The surrogate standard to be used is a mixture of the following representative reference compounds:

- diethylene glycol monobutyl ether;
- diethylene glycol monobutyl ether acetate;
- butanol;
- butyl acrylate;
- 2-ethylhexyl acrylate;
- styrene;
- vinyl acetate.

Weigh, to the nearest 1 mg, about 1 g of each of the reference compounds into a septum-sealable vial using the analytical balance (6.6), adding the high boilers before the low boilers. Remove the cap only to allow each reference compound to be introduced. Add approximately 5 mg to 10 mg of polymerisation inhibitor (7.5) (leading to about a concentration of 1 000 mg/kg of polymerisation inhibitor) to the mixture.

NOTE Evaporation of readily volatile substances during weighing can be reduced by precooling and pipetting the reference compounds.

An example of a chromatogram of the stock reference compound mixture is given in Figure A.1.

7.3 Marker compound

The marker compound n-tetradecane characterizes the upper limit of the VOC range. Its retention time is the end point for integration.

7.4 Citrate buffer, pH 5,0, obtainable commercially in ready for use form or can be prepared in-house by mixing 20,265 g of citric acid and 7,840 g of sodium hydroxide filled up to 1 l with demineralized water (7.1) at 20 °C in a volumetric flask.

7.5 Polymerisation inhibitor, 2,6-di-tert-butyl-4-methylphenol or the acid sodium salt hydrate of *N*,*N*-dimethyldithiocarbamate.

8 Procedure

8.1 Number of determinations

Carry out triplicate determinations of the test sample without standard additions (see 8.2.3) and of each of the four test samples containing standard additions (see 8.2.4).

8.2 Sample preparation

8.2.1 General

Sample preparation involves diluting the sample (see 8.2.2) and preparing the test samples with standard additions (see 8.2.4) and without standard additions (see 8.2.3).

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

Figure 1 shows a diagram of the sample-preparation plan.

8.2.2 Dilution of original sample

Weigh 10 g of the original sample and 10 g of citrate buffer (7.4) to the nearest 0,1 g into a 20 ml septum vial (6.4), seal and mix.

8.2.3 Preparation of test samples for analysis without multiple standard additions

Vigorously shake the sealed septum vial containing the diluted sample (prepared as in 8.2.2), then immediately remove any excess vapour by piercing the septum with a 2 ml disposable syringe (6.3). For the analysis, weigh aliquots of (15 ± 3) mg to the nearest 0,1 mg into each of three vials (6.4) and seal the latter immediately.

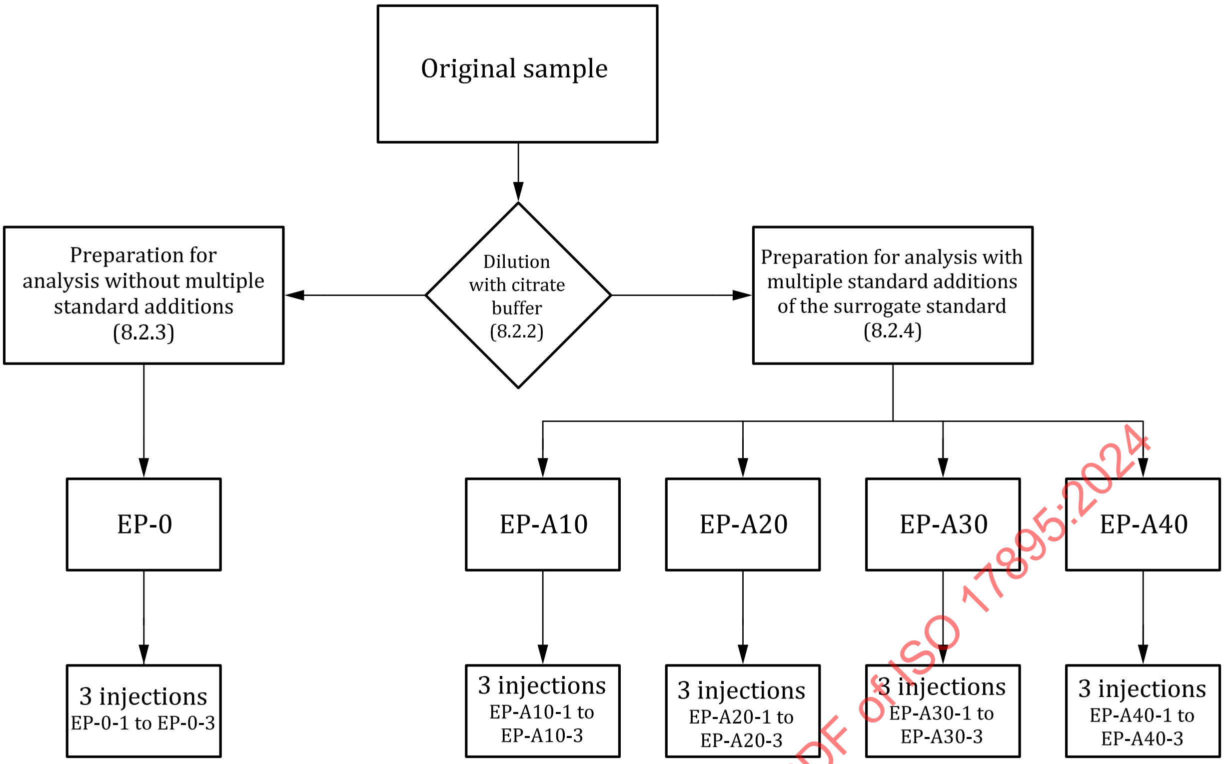
NOTE Higher initial test sample masses result in errors in the result due to the increase in pressure.

8.2.4 Preparation of test samples for analysis with multiple standard additions

Prepare four diluted samples as in 8.2.2 and add, using a 50 µl syringe (6.2), about 10 µl, 20 µl, 30 µl and 40 µl of surrogate standard (7.2) (a different volume to each vial). Note the added amount to the nearest 0,1 mg. Close the vials firmly and mix well.

Shake the sealed vials vigorously once again, then remove any excess vapour by piercing the septum with a 2 ml disposable syringe (6.3). For the analysis, weigh an aliquot of about (15 ± 3) mg of these diluted test samples containing standard additions to the nearest 0,1 mg into each of three empty vials (6.4) and seal the latter immediately.

NOTE If a standard addition for a certain coating matrix is not feasible, another representative coating matrix can be used alternatively for standard addition. Since the slope of the calibration curve is likely to be different when using another matrix, it was necessary to record this deviation in the test report.



Key

0	original sample
A10, A20, A30, A40	standard additions of 10 mg, 20 mg, 30 mg and 40 mg of the stock reference compound mixture
EP	emulsion paint

Figure 1 — Sample-preparation plan

8.3 Analysis

8.3.1 General

Place the vials prepared as in 8.2.3 and 8.2.4 in the headspace injector.

8.3.2 Headspace injector

The following conditions are applied for analysis using aheadscape injector:

Controlled sample temperature: 150 °C.

Controlled transfer line and dispensing valve temperatures: 160 °C.

Temperature hold time: 4 min.

8.3.3 Gas chromatograph

Adjust the gas-chromatographic conditions to the design of the apparatus. Two examples of gas-chromatographic conditions are given in Tables 1 and 2.

Table 1 — Example 1: headspace injector with sample loop

Capillary column:	Length	30 m
	internal diameter	0,32 mm
	coating	95 % dimethylsilicone and 5 % phenylsilicone
	film thickness of coating	about 1 µm
Temperatures:	Injector temperature:	250 °C
	Oven:	Initial temperature: 100 °C
	Heating rate:	10 °C/min
	Final temperature:	280 °C
	Detector temperature:	300 °C
Carrier gas	flow rate	1,8 ml/min
Split	Split ratio:	1:10

Table 2 — Example 2: headspace injector with equal-pressure application method

Capillary column:	Length	30 m
	internal diameter	0,32 mm
	coating	95 % dimethylsilicone and 5 % phenylsilicone
	film thickness of coating	about 1 µm
	film thickness of coating	about 1 µm
	restrictor capillary inserted between column and detector	methyl-deactivated 1,5 m × 0,15 mm
Temperatures:	Injector temperature:	200 °C
	Oven:	Initial temperature: 100 °C
	Heating rate:	10 °C/min
	Final temperature:	280 °C
	Detector temperature:	300 °C
Carrier gas	pressure of headspace p_{HS}	160 kPa
	pressure of GC p_{GC}	125 kPa
	flow rate ϕ:	1,8 ml/min
Split:	Split flow	30 ml/min to 50 ml/min

8.3.4 Determination of integration end point

Determine the retention time of the marker compound by a separate gas chromatogram analysis. It defines the integration end point for the VOC determination.

9 Evaluation

Evaluate the chromatogram by integrating all the peaks to obtain their sum up to the retention time of tetradecane.

In determining the peaks, the signal/noise ratio may be at least 5:1 for the peak to be included in the integration.

The accuracy of the determination in the standard addition method is substantially affected by the precision with which the samples are weighed into the vials. To avoid losses due to premature evaporation, it is essential to work quickly. For this reason, sample masses of 15 mg can only be reproduced approximately in practice, and it is therefore desirable to normalize the peak areas of each analysis to 1 mg by dividing them by the actual sample mass and using Formula (1):

$$A_{\text{norm}} = \frac{A}{m_{\text{vd}} \times \frac{m_{\text{p}}}{m_{\text{p}} + m_{\text{cb}}}} \quad (1)$$

where

A_{norm}	is the area normalized to 1 mg of sample, in area units/milligram;
A	is the integrated area, in area units, determined up to and including the retention time of the marker compound;
m_{vd}	is the mass, in milligrams, of the test sample (EP-0-1 to EP-A40-3, see Figure 1);
m_{p}	is the mass, in grams, of the original sample of emulsion paint (EP);
m_{cb}	is the mass, in grams, of citrate buffer added to the original sample.

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.

For in-can VOC content lower than the limit of quantification of 100 milligram per kilogram, state: "< 100 mg/kg" when reporting results.

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

First calculate, from the normalized areas, A_{norm}, the mean, $\bar{A}_{\text{norm}(x)}$, in area units/milligram, of the three analyses made on the test samples without a standard addition and those made on each set of three test samples with a standard addition of 10 mg, 20 mg, 30 mg and 40 mg, using Formula (2):

$$\bar{A}_{\text{norm}(x)} = \frac{1}{3} \times \sum_{i=1}^{3} A_{\text{norm}(x)} \quad (2)$$

where

$A_{\text{norm}(x)}$	is the area, normalized to 1 mg of emulsion paint, of the test samples without standard additions and of those with standard additions of 10 mg, 20 mg, 30 mg or 40 mg, expressed in area units per milligram;
x	is the subscript 0, 10, 20, 30 or 40 for the test samples with standard additions of 0 mg, 10 mg, 20 mg, 30 mg and 40 mg, respectively.

Then carry out a linear regression analysis either by calculation or, alternatively, by calculation and plotting the mean area obtained in this way against the associated standard addition, as shown in Formula (3):

$$y = b_x \times x + A_y \quad (3)$$

where

y is the area $A_{\text{norm}}(_x)$, expressed in area units/mg for the test samples with and without standard addition;

b_x is the mass, expressed in grams, of the original sample;

A_y is the intercept of the linear regression plot with the vertical axis;

x is the amount of added mass of the standard addition, expressed in units of mg.

For $y = 0$, the amount, m_{voc}, in milligrams, of VOC in the original sample mass, m_{S}, can be calculated from the intercept, a_y, on the vertical axis and the slope, b, of the linear regression plot (see Figure 2), using Formula (4):

$$m_{\text{VOC}} = \frac{A_y}{b} \tag{4}$$

The in-can VOC content, f_{VOC}, in milligrams per kilogram, is then given by Formula (5):

$$f_{\text{VOC}} = \frac{m_{\text{VOC}}}{m_{\text{S}}} \times 1\,000 \tag{5}$$

where

f_{VOC} is the in-can VOC content, f_{VOC}, expressed in milligrams per kilogram;

m_{VOC} is the amount, m_{VOC}, expressed in milligrams, of VOC;

m_{S} is the mass, expressed in grams, of the original sample.

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

The conversion to the in-can VOC content in grams per litre, ρ_{VOC}, requires a knowledge of the density of the emulsion paint, which shall either be obtained from the manufacturer's information or be determined by one of the methods specified in ISO 2811-1, ISO 2811-2, ISO 2811-3 or ISO 2811-4. In arbitration cases, the value determined as specified in ISO 2811-1 shall be regarded as final.

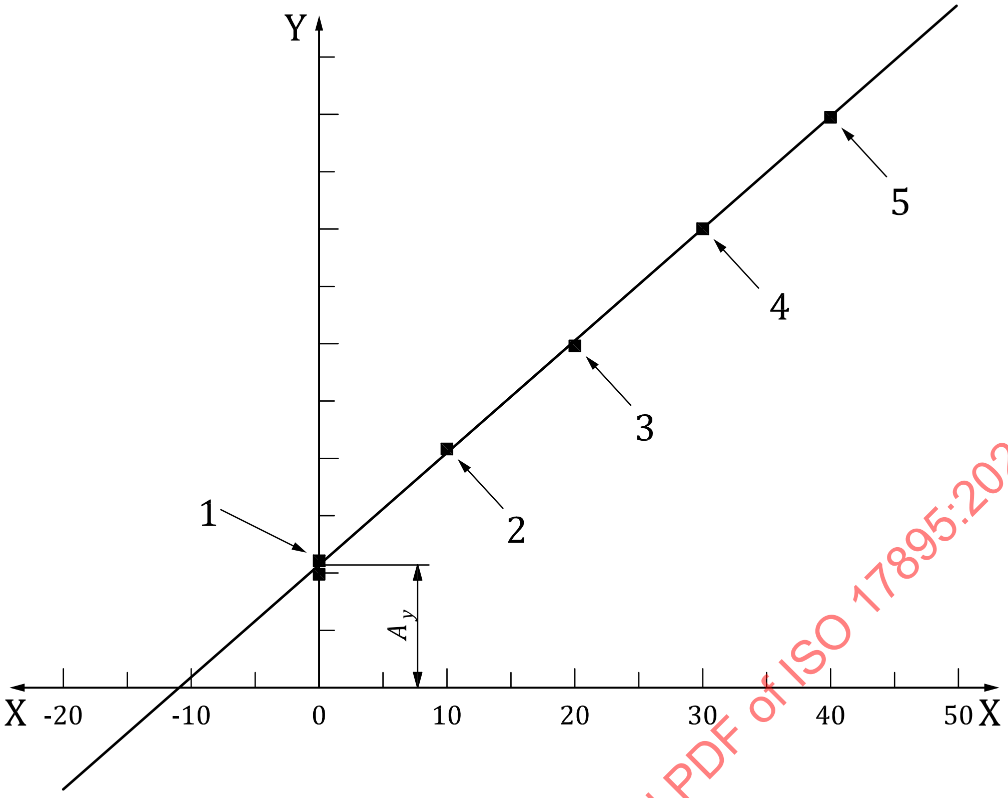
To carry out the conversion, use Formula (6):

$$\rho_{\text{VOC}} = \frac{f_{\text{VOC}} \times \rho_{\text{S}}}{1\,000} \tag{6}$$

where

ρ_{VOC} is the in-can VOC content, expressed in gram per litre;

ρ_{S} is the density, expressed in grams per millilitre, of the original sample.



Key

X	standard addition, in mg
Y	$A_{\text{norm}}(x)$, in area units/mg
1	test samples EP-0-1 to EP-0-3 (without additions) (see also Figure 1)
2	test samples EP-A10-1 to EP-A10-3 (10 mg standard addition) (see also Figure 1)
3	test samples EP-A20-1 to EP-A20-3 (20 mg standard addition) (see also Figure 1)
4	test samples EP-A30-1 to EP-A30-3 (30 mg standard addition) (see also Figure 1)
5	test samples EP-A40-1 to EP-A40-3 (40 mg standard addition) (see also Figure 1)
A_y	intercept of the linear regression plot with the vertical axis

Figure 2 — Linear regression plot

11 Precision

11.1 General

Four different interlaboratory studies were conducted in eight laboratories. The following results shown in 11.2 and 11.3 were obtained.

11.2 Repeatability limit, *r*

The repeatability limit, *r*, is the value below which the absolute difference between two single test results, obtained on identical material by one operator in one laboratory within a short interval of time using the standardized test method, can be expected to lie. For this method, *r* is 10 %, with a 95 % probability.

11.3 Reproducibility limit, *R*

The reproducibility limit, *R*, is the value below which the absolute difference between two test results, obtained on identical material by operators in different laboratories using the standardized test method, can be expected to lie. For this method, *R* is 30 %, with a 95 % probability.

12 Test report

The test report shall contain at least the following information:

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

b) information on the sample preparation;

c) a reference to this document (ISO 17895:2024);

d) the gas-chromatographic conditions used for the analysis;

e) the in-can VOC content, in milligrams per kilogram (rounded to the nearest 100 milligram per kilogram) or grams per litre (rounded to the nearest 0,1 gram per litre), as specified in Clause 10; including indication of the experimental method used;

f) any deviations from the test method specified;

g) any unusual features observed;

h) items which were agreed between the interested parties;

i) the date of the test.