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Paints and varnishes — Determination of the volatile organic compound content of low-VOC emulsion paints (in-can VOC)

Peintures et vernis — Détermination du contenu en composés organiques volatiles dans des peintures en émulsion à faible teneur en COV (COV en récipient)

Reference number
ISO 17895:2005(E)

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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 17895 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*.

Introduction

The requirements imposed today by authorities, for health and environmental reasons, include the assessment of the content of residual monomers and organic saturated volatiles, sometimes down to minute traces.

This International Standard is one of a series of standards dealing with the VOC content of paints, varnishes and related products: ISO 11890-1 (see the Bibliography) specifies a method for determining VOC contents greater than 15 % (by mass), ISO 11890-2 is applicable to VOC contents between 0,1 % and 15 % (by mass).

This International Standard describes a method for determining VOC contents between 0,01 % and 0,1 % (by mass). In contrast to ISO 11890-1 and ISO 11890-2, this standard is applicable to volatile organic compounds with boiling points up to 250 °C.

Paints and varnishes — Determination of the volatile organic compound content of low-VOC emulsion paints (in-can VOC)

1 Scope

This International Standard specifies a gas-chromatographic method of quantitatively determining the volatile organic compound (VOC) content (i.e. the content of organic compounds with boiling points up to 250 °C) under standard conditions (101,325 kPa) of low VOC content emulsion paints (in-can VOC). The method is applicable to VOC contents between 0,01 % and 0,1 % (by mass).

The main purpose of the method is to qualify low-VOC emulsion paints, not routine quality control.

2 Normative references

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

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]

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 The properties and the amounts of 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[1] or by agreement.

[ISO 4618]

3.3
in-can VOC

volatile organic compound present in a water-based emulsion paint

3.4
emulsion paint
latex paint

coating material in which the organic binder is an aqueous dispersion

[ISO 4618]

3.5
full evaporation

method of transferring the VOCs in a liquid sample from the liquid to the vapour phase

NOTE Although a headspace injector with septum-sealable vials is used for introduction of a test portion of the vapour phase into the chromatographic column, the full evaporation method differs substantially from conventional headspace analysis in which equilibrium is established. Since the vial contains very small amounts of sample, virtually all the VOCs enter the vapour phase when heated to a certain temperature [3].

3.6
stock reference compound mixture

mixture prepared from pure substances for use in the standard addition method

NOTE The concentration of the stock reference compound mixture is determined by the initial masses of the individual components in the sample and their degree of purity.

3.7
multiple standard addition method

method of determining the VOC content in which a known amount of stock reference compound mixture is added to the sample

4 Principle

The VOCs in a very small amount of 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 buffer solution are heated to 150 °C in a septum-sealed vial and, 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 tetradecane (boiling point 252,6 °C) are integrated. Standard additions of a stock reference compound mixture (see 3.6) are employed at four

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[1] For the purposes of this International Standard, the applicable regulations are given in European Commission decision 96/13/EC dated 1996-01-06 which defines all organic compounds having a boiling point (or initial boiling point) of not more than 250 °C at normal pressure (101,325 kPa) as volatile organic compounds (VOCs).

concentration levels to determine the VOC content. The result is based on the average response factor of the reference compound mixture.

NOTE Determination of individual components in the sample, or of standards prepared separately from emulsions or emulsion paints which are as free of VOCs as possible, can be used to validate the analytical system.

5 Apparatus

Ordinary laboratory apparatus and glassware, together with the following:

5.1 Gas chromatography system, consisting of a headspace injector, preferably with an automatic sample changer, a temperature-programmable gas chromatograph suitable for capillary gas chromatography, a flame-ionization detector or mass-selective detector and a data evaluation system. All the components of the headspace injector which come into contact with the sample (e.g. dispensing needle, dispensing valve, transfer tube) shall be capable of being heated.

5.2 Non-polar fused-silica capillary column, 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.

5.3 Microlitre syringe, of capacity 50 µl.

5.4 2 ml disposable plastic syringe.

5.5 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 International Standard result in fairly high pressures in the vials, care shall be taken to ensure that they are tightly sealed.

5.6 Volumetric flask, of capacity 1 l.

5.7 Analytical balance, accurate to 0,1 mg.

5.8 Top-pan balance, accurate to 0,1 g.

5.9 Refrigerator, for storing the reference compounds.

6 Reagents and materials

Unless otherwise specified, use only reagents of recognized analytical grade (purity greater than 99 %) and only grade 1 water as defined in ISO 3696.

6.1 Gases:

- **Carrier gas**: dry, oxygen-free helium, nitrogen or hydrogen having a purity of at least 99,995 % (by volume).
- **Detector gas mixture**: hydrogen having a purity of at least 99,995 % (by volume) and synthetic air free of organic compounds.

6.2 Stock reference compound mixture, containing 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 (5.7), adding the high boilers before the low boilers. Remove the cap only to allow each reference compound to be introduced. Add about 1 000 mg/kg polymerization inhibitor (6.4) 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 Annex A.

6.3 Citrate buffer, pH 5,0: obtainable commercially in ready-to-use form or can be prepared in-house by making up 20,265 g of citric acid and 7,840 g of sodium hydroxide to 1 l at 20 °C with deionized water in a volumetric flask.

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

6.5 Tetradecane, with a purity of at least 99,5 % (by mass).

7 Sampling

Take a representative sample of the product to be tested, as described in ISO 15528.

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 of emulsion paint (see 8.2.2) and preparing the test samples with and without standard additions (see 8.2.4 and 8.2.3, respectively).

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.

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

8.2.2 Dilution of original sample

Weigh 10 g of the original sample (emulsion paint) and 10 g of citrate buffer (6.3) to the nearest 0,1 g into a 20 ml septum vial (5.5), seal and mix.

8.2.3 Preparation of test samples for analysis without multiple standard additions

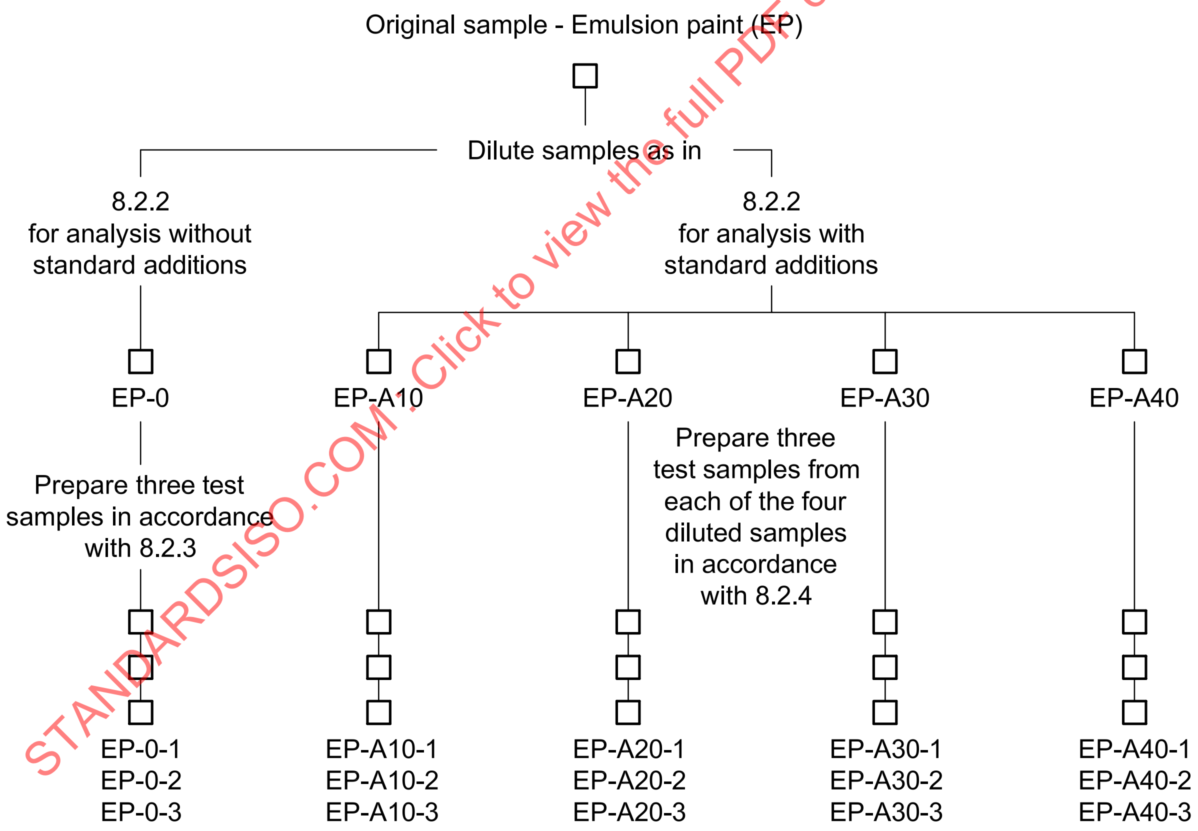
Vigorously shake the sealed septum vial containing the diluted sample of emulsion paint (prepared as in 8.2.2), then immediately remove any excess vapour by piercing the septum with a 2 ml disposable syringe (5.4). For the analysis, weigh aliquots of (15 ± 3) mg to the nearest 0,1 mg into each of three vials (5.5) and seal the latter immediately.

NOTE Higher initial test sample masses will 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 of emulsion paint as in 8.2.2 and add, using a 50 µl syringe (5.3), about 10 µl, 20 µl, 30 µl and 40 µl of stock reference compound mixture (6.2) (a different volume to each vial). Weigh each vial 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 (5.4). 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 (5.5) and seal the latter immediately.



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

Figure 1 — Sample-preparation plan

8.3 Analysis

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

8.3.1 Headspace injector

Controlled sample temperature: 150 °C;

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

Temperature hold time: 4 min.

8.3.2 Gas chromatograph

Adjust the gas-chromatographic conditions to the design of the apparatus. Two examples of this are given below.

EXAMPLE 1 Headspace injector with sample loop

Capillary column: Length 30 m, internal diameter 0,32 mm, coated with 95 % dimethylsilicone and 5 % phenylsilicone (film thickness 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 ratio: 1:10

EXAMPLE 2 Headspace injector with equal-pressure application method

Capillary column: Length 30 m, internal diameter 0,32 mm, coated with 95 % dimethylsilicone and 5 % phenylsilicone (film thickness about 1 µm), joined to a methyl-deactivated 1,5 m × 0,15 mm restrictor capillary inserted between column and detector

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 flow rate: About 1,8 ml/min, equivalent to pressure settings of $p_{\text{headspace}}$ = 160 kPa, p_{GC} = 125 kPa

Split: Split flow 30 ml/min to 50 ml/min

8.4 Determination of integration end point

Determine the retention time of tetradecane by a separate GC analysis. It defines the integration end point for the VOC determination.

9 Evaluation

9.1 Peak area determination

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

NOTE In determining the peaks, the signal/noise ratio should 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 the equation:

$$A_{\mathrm{norm}} = \frac{A}{m_{\mathrm{vd}} \times \dfrac{m_{\mathrm{p}}}{m_{\mathrm{p}} + m_{\mathrm{cb}}}}$$

where

A_{norm}	is the area normalized to 1 mg of emulsion paint, in area units/milligram;
A	is the integrated area, in area units, determined up to the retention time of tetradecane;
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.

9.2 Calculation of in-can VOC content

First calculate, from the normalized areas, A_{norm}, the mean, $\overline{A}_{\mathrm{norm}(x)}$, 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 the equation:

$$\overline{A}_{\mathrm{norm}(x)} = \frac{1}{3} \times \sum_{i=1}^{3} A_{\mathrm{norm}(x)}$$

where

$A_{\mathrm{norm}(x)}$	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, 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.

From the intercept, A_y, on the vertical axis and the slope, B, of the linear regression plot (see Figure 2), calculate the amount, m_{voc}, in milligrams, of VOC in the original sample mass, m_p, using the equation:

$$m_{VOC} = \frac{A_y}{B}$$

The in-can VOC content, w_{VOC}, in milligrams per kilogram, is then given by:

$$w_{VOC} = \frac{m_{VOC}}{m_p} \times 1000$$

where m_p is the mass, in grams, of the original sample of emulsion paint (EP).

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 can either be obtained from the manufacturer's information or be determined by one of the methods specified in ISO 2811-1 to 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 the following equation:

$$\rho_{VOC} = \frac{w_{VOC} \times \rho_{EP}}{1000}$$

where

w_{VOC} is the in-can VOC content, in milligrams per kilogram (% by mass);

ρ_{EP} is the density, in grams per millilitre, of the original sample of emulsion paint.

10 Precision

10.1 General

Four different interlaboratory studies were conducted in eight laboratories. The following results were obtained:

10.2 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, may be expected to lie. For this method, r is 10 %, with a 95 % probability.

10.3 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, may be expected to lie. For this method, R is 30 %, with a 95 % probability.