INTERNATIONAL STANDARD

ISO 11890-2

Fourth edition
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Paints and varnishes — Determination of volatile organic compounds(VOC) and/or semi volatile organic compounds (SVOC) content —

Part 2:
Gas-chromatographic method

Peintures et vernis — Détermination de la teneur en composés organiques volatils (COV) et/ou composés organiques semi-volatils (COSV) —

Partie 2: Méthode par chromatographie en phase gazeuse

Reference number
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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: 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.

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 documents 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).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, 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 fourth edition cancels and replaces the third edition (ISO 11890-2:2013), which has been technically revised.

The main changes compared to the previous edition are as follows:

— the scope has been expanded to include the determination of semi volatile organic compounds (SVOC);

— the scope has been expanded to include concentration ranges from 0,01 % to 100 %;

— the specifications for determination of semi-volatile organic compounds have been added.

A list of all parts in the ISO 11890 series can be found on the ISO website.

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.

Introduction

This document is one of a series of standards dealing with the sampling and testing of coating materials and their raw materials. It specifies a method for the determination of the volatile organic compounds (VOC) content and the semi-volatile organic compounds (SVOC) content of coating materials and their raw materials.

Paints and varnishes — Determination of volatile organic compounds(VOC) and/or semi volatile organic compounds (SVOC) content —

Part 2:
Gas-chromatographic method

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 is applicable for the determination of VOC and SVOC with an expected VOC and/or SVOC content greater than 0,01 % by mass up to 100 % by mass.

The method given in ISO 11890-1 is used when the VOC is greater than 15 % by mass. This document (method ISO 11890-2) applies when the system contains VOC and SVOC as the VOC result of ISO 11890-1 can be influenced by the SVOC. For VOC content smaller than 0,1 %, the head space method described in ISO 17895 is used as an alternative. ISO 11890-1 and ISO 17895 cannot be used for the determination of the SVOC content.

NOTE 1 Some ingredients of coating materials and their raw materials can decompose during analysis and cause artificial VOC and/or SVOC signals. When determining VOC and/or SVOC for coating materials and their raw materials, these signals are artefacts of the method and are not taken into account (examples are given in Annex B).

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. The method defined in this document is not applicable for determination of water content.

NOTE 2 If organic acids or bases and their corresponding salts are present in the coating material or its raw materials, the amount that is quantified by this method might not be accurate due to a change in the acid or base equilibrium.

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 760, *Determination of water — Karl Fischer method (General method)*

ISO 1513, *Paints and varnishes — Examination and preparation of test samples*

ISO 2811 (all parts), *Paints and varnishes — Determination of density*

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.

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

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

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 compounds content (VOC content)* (3.4).

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* (3.6).

[SOURCE: ISO 4618:2014, 2.270]

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: As to current usage of the term SVOC in the field of coating materials, see *semi-volatile organic compounds content (SVOC content)* (3.5).

3.3
non-volatile organic compound
NVOC
organic liquid and/or solid not classified as *VOC* or *SVOC*

3.4
volatile organic compounds content
VOC content
VOCC
mass of the *volatile organic compounds* (3.1) 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, 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 or non-volatile organic compounds.

[SOURCE: ISO 4618:2014, 2.271, modified — Note 2 to entry has been added.]

3.5
semi-volatile organic compounds content
SVOC content
SVOCC
mass of the *semi-volatile organic compounds* (3.2) 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 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 those with boiling points below and including the upper and above the lower limit, and compounds with higher boiling points are considered to be non-volatile organic compounds.

3.6
exempt compound
organic compound that does not participate in atmospheric photochemical reactions

Note 1 to entry: This expression is only relevant in some countries.

3.7
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

3.8
internal standard
compound which is not present in the sample, is completely separated from the other components in the chromatogram, is inert with respect to the sample constituents, stable in the required temperature range and of known purity and which is added to the sample to control the dilution and the injection step of the analysis

3.9
surrogate standard
compound of known purity which is used to quantify unidentified VOCs and SVOCs

3.10
marker compound
compound which is used to differentiate between VOC and SVOC, or SVOC and NVOC if the differentiation has to be made on the basis of *retention time* (3.11)

3.11
retention time
t_R
time elapsed from injection of the sample component to the recording of the peak maximum

3.12
extraction solvent
liquid used to extract the VOCs and SVOCs from the matrix under investigation

3.13
major peak
peak that contributes significantly to either

— the VOC content, i.e. ≥ 10 % of the absolute VOC content (as DEA equivalent) and ≥ 0,1 % by mass (as DEA equivalent), or

— the SVOC content, i.e. ≥ 10 % of the absolute SVOC content (as DEA equivalent) and ≥ 0,1 % by mass (as DEA equivalent)

3.14

minor peak

peak that contributes only to a minor extent to either

- the VOC content, i.e. < 0,1 % by mass (as DEA equivalent) and/or < 10 % of the absolute VOC content (as DEA equivalent), or
- the SVOC content, i.e. < 0,1 % by mass (as DEA equivalent) and/or < 10 % of the absolute SVOC content (as DEA equivalent)

3.15

reagent

substance used in chemical/biochemical analysis or other reactions

[SOURCE: ISO 20391-1:2018, 3.19]

4 Principle

After preparation of the sample, the VOCs, SVOCs and NVOCs 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, e.g. via GC-MS, they are quantified from the peak areas with respect to their compound specific relative response with the help of an internal standard, via GC-FID. Non-identifiable substances are quantified with respect to a surrogate standard that can be identical to the internal standard. A calculation is performed to give the VOC and/or SVOC content of the sample.

5 Required information

For any particular application, 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.

The required information can include the following points:

a) the organic compound(s) to be determined (see Clause 9);

b) the experimental conditions to be used (see 8.5);

c) the classification criteria for VOC and/or SVOC;

d) which of the organic compounds in a) are exempt compounds (if relevant);

e) the method of calculation to be used (see Clause 10 and Clause 11).

6 Apparatus

6.1 Gas chromatograph

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.

Use one of the two types specified in 6.1.1 and 6.1.2.

6.1.1 Hot-injection system (preferred system)

The instrument shall have a variable-temperature injection block with sample splitter. The injection temperature shall be capable of being set to an accuracy of 1 °C. Standard operating temperature shall be between 250 °C and 280 °C.

NOTE It is useful to use silanized glass wool to retain non-volatile constituents. The active sides of silanized glass wool can be a sink for organic compounds and significantly influence the recovery rate in the lower range of the method. The occurrence of adsorption is revealed by peak tailing, in particular with components of low volatility and/or high polarity.

6.1.2 Cold-injection system (programmed temperature vaporizer, PTV)

The cold-injection system shall be provided with temperature programming for heating from ambient to 300 °C including a sample splitter for split operation.

NOTE It is useful to use silanized glass wool to retain non-volatile constituents. The active sides of silanized glass wool can be a sink for organic compounds and significantly influence the recovery rate in the lower range of the method. The occurrence of adsorption is revealed by peak tailing, in particular with components of low volatility and/or high polarity.

6.1.3 Selection of sample injection system

The choice between hot-injection and cold-injection will depend on the type of product under test. It is preferred to use the cold-injection system for products which, at high temperature, release substances which interfere with the determination. Cleavage products of binders or additives can be reduced by the use of cold injection system.

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 (see Annex B).

6.2 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 6.4).

6.3 Detector

The following two detectors shall be used.

6.3.1 Mass spectrometer or other mass-selective detector (MS or MSD), for the identification of VOC and SVOC compounds. To prevent condensation, the detector temperature shall be at least 10 °C above the maximum oven temperature.

6.3.2 Flame ionization detector (FID), for quantification of VOC and SVOC 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.

6.4 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 5 % phenyl-modified poly(dimethylsiloxane) or 6 % (cyanopropyl-phenyl)-methylpolysiloxane at a suitable film thickness shall be used.

NOTE Columns such as DB-5, HP-5, or DB-1301 are suitable[1]. DB-5, HP-5 or DB-1301 are GC columns characterized as equivalent to USP phase G27 or G43. Other columns equivalent USP phase G27 or G43, which meet the pre-set performance criteria of this method can be used as well.

6.5 Analytical system performance criteria

The analytical system performance criteria shall be demonstrated. The limit of quantification (LOQ) for the VOC content and SVOC content, respectively, is 0,01 % by mass. For single compounds, the LOQ is assumed to be 0,005 % by mass using the response factor for diethyladipate (i.e. in DEA equivalents).

NOTE The limit of quantification can deviate for single compounds. If necessary, the compound specific limit of quantification can be determined for the considered single compound(s).

Chromatographic resolution shall be sufficient to separate the compounds DEA and tetradecane (C14), as well as docosane (C22) and dibutylsebacate (DBS). At least a resolution of 1 shall be reached.

For the quantification of VOC content and/or SVOC content at concentrations below 0,1 % by mass the LOQ of triethylene glycol (TEG) shall be proven to be at least 0,005 % by mass, based on the sample weight.

6.6 Qualitative-analysis equipment

If the separated components are to be identified by a mass-selective detector, the instrument shall be coupled to the gas chromatograph.

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 Data processing

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

6.9 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)].

6.10 Gas filters

Filters shall be installed in the gas chromatograph connection pipes to adsorb residual impurities in the gases (6.11).

6.11 Gases

6.11.1 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-5, HP-5 and DB-1301 are the trade names of products. This information is given for the convenience of users of this document 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.

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

6.11.3 Auxiliary gas, nitrogen or helium of the same quality as the carrier gas.

7 Reagents

7.1 General

Table 1 shows the surrogate standard as well as a non-exhaustive list of an internal standard, markers, performance criteria compounds and extraction solvents.

Table 1 — List of reagents and their function

Reagent	CAS – No.	Abbreviation	Function
n-docosane	CAS 629-97-0	C22	SVOC marker compound
dibutylsebacate	CAS 109-43-3	DBS	Performance criteria compound
n-tetradecane	CAS 629-59-4	C14	
triethylene glycol	CAS 112-27-6	TEG	
diethyladipate	CAS 141-28-6	DEA	VOC marker compound/ internal standard/surrogate standard
acetonitrile	CAS 75-05-8	ACN	Extraction solvent
methanol	CAS 67-56-1	MEOH	
tetrahydrofuran	CAS 109-99-9	THF	

7.2 Internal standard

The internal standard should be a compound which is not present in the sample and is completely separated from the other components in the chromatogram. It shall be inert with respect to the sample constituents, stable in the required temperature range, and of known purity. The preferred internal standard is DEA.

It has been observed that DEA is not chemically stable in alkaline matrices when the solvent methanol is used. If reaction of DEA in a matrix is suspected, choose another suitable solvent or another internal standard.

NOTE 1 The benefit of using DEA as internal standard is that only one compound needs to be added during analysis fulfilling the function as surrogate standard (7.3), marker compound (7.4) and internal standard.

NOTE 2 If DEA is not suitable as internal standard, internal standards such as glycol ethers can be suitable.

7.3 Surrogate standard

The surrogate standard to be used is DEA.

7.4 Marker compound

In case of the need of a classification according to 9.2, marker compounds may be used to classify unidentified components as VOC or SVOC via retention time. If a peak cannot be identified, its boiling point will be unknown. In this case, the marker compound to characterize the upper limit of the VOC range is DEA and the marker compound to characterize the upper limit of the SVOC range is C22, if not otherwise specified by the contractor, i.e. any valid legislation, label or a classification.

7.5 Performance criteria compounds

The performance criteria compounds are used to prove sufficient chromatographic resolution at the retention time of the marker compounds. They are also used to ensure that the analytical system has a sufficient sensitivity.

7.6 Calibration compounds

The compounds used for calibration shall have a purity of at least a 99 % by mass or shall be of known purity. In the latter case, a correction with respect to purity shall be applied.

7.7 Extraction solvent

The extraction solvent should be suitable to completely extract the VOCs and SVOCs from the sample under investigation. Methanol, acetonitrile and THF have been proven to be suitable extraction solvents. The extraction solvent 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.

The suitability of a solvent or solvent mixture other than methanol, acetonitrile and THF shall be checked by determining the recovery rates of analytes from the sample under investigation.

8 Procedure

8.1 Sampling

Prepare the sample as specified in ISO 1513 for testing in the “ready for use” state.

Take at least duplicate representative samples of the product to be tested (or of each product in the case of a multi-coat system), as specified in ISO 15528 and prepare each sample for testing.

8.2 Analysis

8.2.1 Sample preparation

Weigh a suitable amount of sample greater than 0,2 g (generally 1 g to 3 g is recommended) and an appropriate amount of the internal standard into a sample vial. Dilute the test sample with a suitable volume of extraction solvent (typically a dilution factor of 4 to 50 is applied, depending on the target compound concentration, see 7.7), seal the vial and homogenize the contents. When necessary, use methods such as stirring, vortexing or ultrasonic mixing to support extraction. If particles do not readily settle, phase cleaning can be obtained by centrifugation or filtration.

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

Repeat the procedure and perform at least a duplicate analysis.

8.2.2 Data acquisition for sample measurement

Set the instrumental parameters as optimized during calibration.

Determine the retention times of the marker compounds (see 9.2). These retention times define the integration end-point for the unidentifiable VOC and/or SVOC determination in the chromatogram if no other specifications are given.

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 and allocate each peak to the VOC range or to the SVOC range as specified in 9.2.

8.3 Calibration

8.3.1 General

Where suitable calibration compounds are commercially available, the relative response factor shall be determined using multi point calibration.

8.3.2 Preparation of calibration solutions

Weigh, into a sample vial (6.9), to the nearest 0,1 mg, suitable amounts of the compounds determined in 9.1 which are of the same order of magnitude as their respective contents in the product under test.

Weigh a similar amount of the internal standard (7.2) into the sample vial, dilute the mixture with extraction solvent (see 7.7), and inject it under the same conditions as will be used for the test sample.

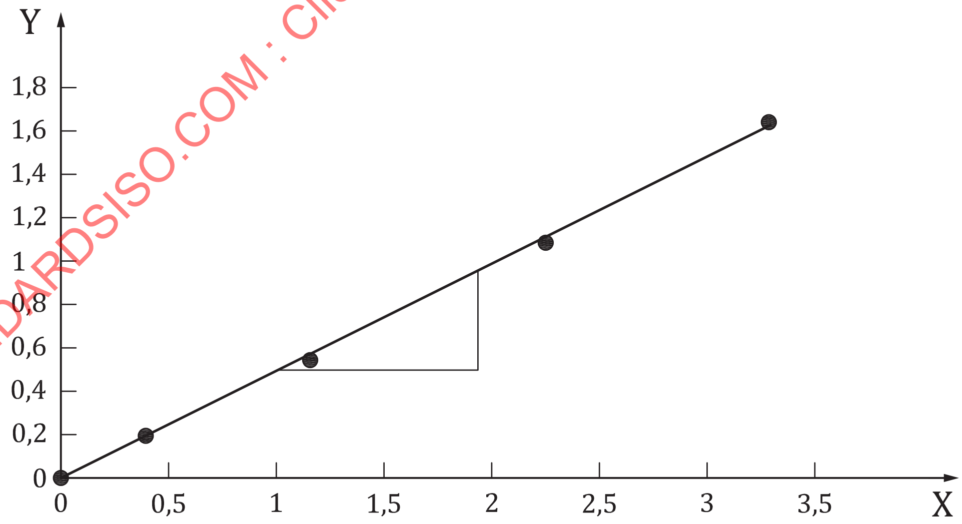
Repeat the procedure above two to seven times depending on the number of calibration points with different amounts, encompassing the respective contents in the product under test.

NOTE 1 Usually, a three- or five-point calibration is suitable.

NOTE 2 A one-point calibration is not suitable for the initial calibration of a compound because it does not allow to verify the linear relation between relative response and relative mass, see Figure 1.

8.3.3 Analysis of the multi-point calibration

Inject suitable amounts of the calibration solutions into the gas chromatograph. Plot the mass of the compound under investigation relative to the internal standard mass versus the peak area of compound *i* divided by the peak area of the internal standard.



Key

Y A_i/A_{is}

X m_i/m_{is}

Figure 1 — Example of a multi-point calibration

Then carry out a linear regression to determine the slope of the curve, s_i . It represents the reciprocal of the compound specific relative response factor (CSRF), r_i. The function for linear regression, the relation between the slope of the curve and the CSRF and the calculation of the relative response factor, r_i, are given in the Formulae (1), (2) and (3).

$$\Delta\left(\frac{A_i}{A_{\text{is}}}\right) = s_i \cdot \Delta\left(\frac{m_i}{m_{\text{is}}}\right) \tag{1}$$

$$r_i = \frac{1}{s_i} \tag{2}$$

$$r_i = \frac{\Delta\left(\frac{m_i}{m_{\text{is}}}\right)}{\Delta\left(\frac{A_i}{A_{\text{is}}}\right)} \tag{3}$$

where

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

s_i is the slope of the curve;

A_i is the peak area of compound i;

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

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

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

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

8.4 Quality assurance

Quality assurance may be used to check if the CSRF has changed and if a new calibration is necessary. An appropriate, e.g. mid level, calibration solution can be used (see 8.3.2).

8.5 Gas chromatographic conditions

The gas-chromatographic conditions used depends on the product to be analysed and shall be optimized each time using a known calibration mixture.

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.

Examples of suitable GC method conditions are given in Annex C.

8.6 Density

If required by the calculation (see 11.3 to 11.5), 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.

8.7 Water content

If required by the calculation (see 11.4 and 11.5), 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, they shall be determined qualitatively (see 9.1).

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 is, in this case, assumed to be zero.

9 Data analysis

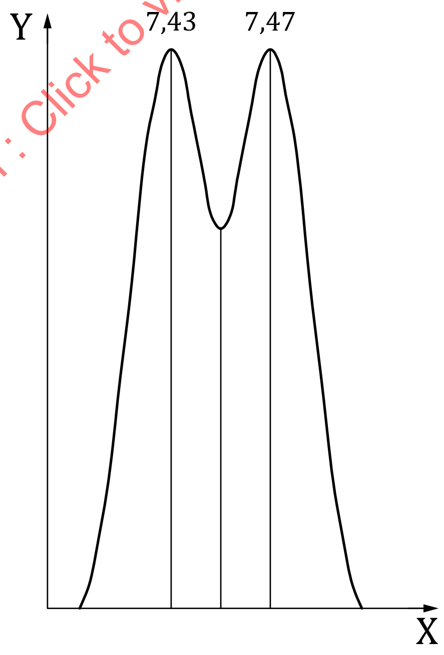
9.1 Integration and identification of compounds

If the organic compounds in the product are not specified, then identify them. A gas chromatograph coupled to a mass-selective detector as specified in Clause 6 shall be used.

Where compounds shall be quantified, peaks of compounds larger than 0,01 % by mass determined with respect to the surrogate standard shall be identified by mass selective detection.

For quantification, evaluate the chromatogram obtained from the FID by integrating all peaks larger than 0,005 % by mass with respect to DEA equivalents.

The peak area for each identified compound in the sample should fall within the area range of the appropriate calibration line. In case the peak area of an identified compound falls outside the calibration line, the calibration line should be extended so that the peak area of the compound in the sample falls within the area range of the calibration line or the sample shall be diluted. In the event that co-eluting peaks remain unresolved, all major peaks shall be identified and the entire affected chromatographic area quantified by dropping perpendiculars to baseline in the valleys between the major peaks (see Figure 2).



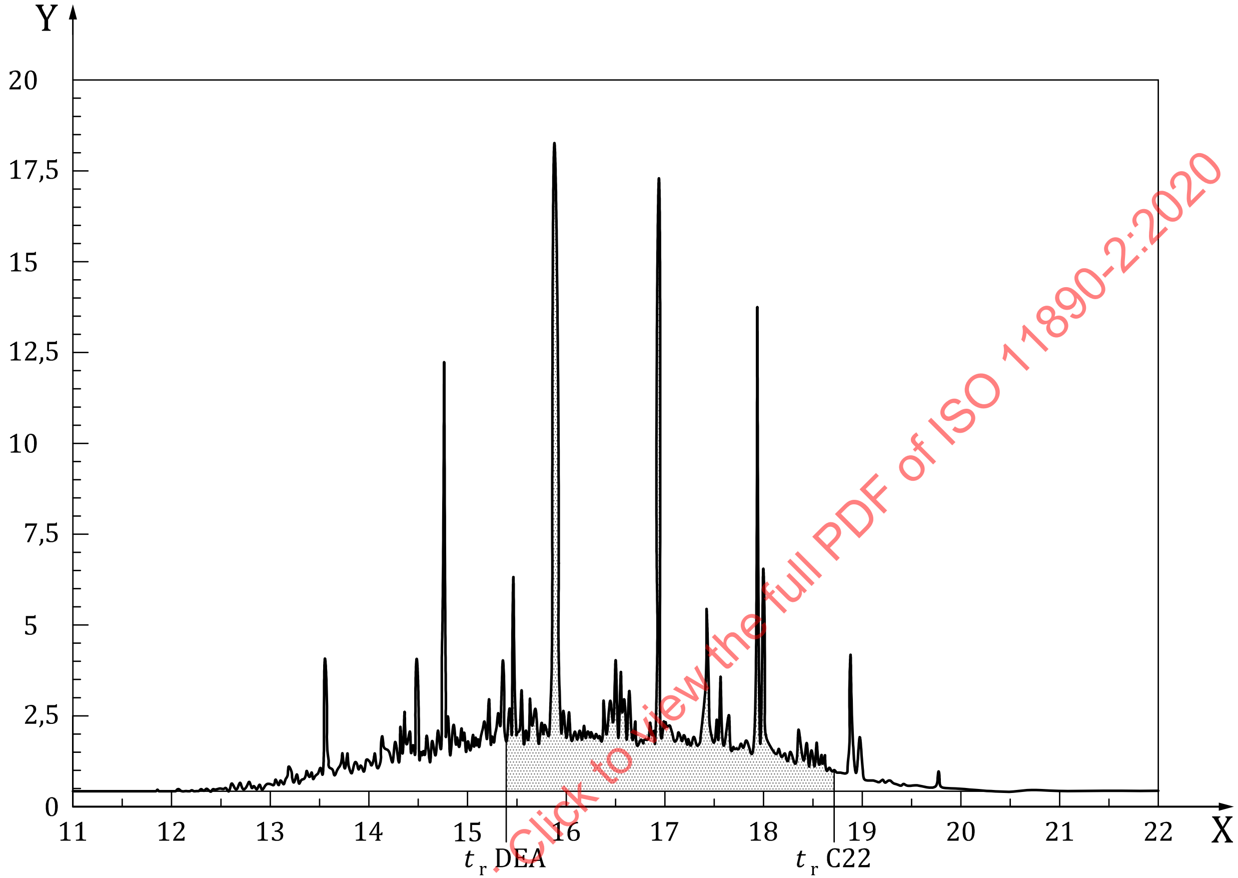
NOTE Source: EN 16402:2019, Figure 1

Figure 2 — Illustration of appropriate integration method for chromatographic components that cannot be resolved

For complex chromatograms that show clusters of peaks that cannot be resolved, these clusters should not be separated into solitary peaks, but the total area of the whole agglomerate should be calculated and quantified using the most appropriate relative response factor (for a group of target compounds).

Such appropriate response factor can be derived from calibration with a compound that, based on its chemical structure, is expected to have the same FID response as the identified cluster components.

Typical clusters could originate from technical mixtures such as hydrocarbons or glycols (see Figure 3). Clusters that span over the marker at the VOC/SVOC-border shall be split into a VOC- and an SVOC-part with a perpendicular to the baseline at the retention time of the marker used.



Key

X retention time in minutes

Y signal in millivolt

Figure 3 — Illustration of appropriate integration method for complex mixtures of chemical homologues that cannot be resolved

In isomeric mixtures, different isomers of the same compound often elute at different retention times due to different interactions with the column material. Therefore, isomeric mixtures can appear as more than one peak in the chromatogram.

If the isomers have different boiling points, e.g. isomers of xylene, they should be identified, classified by their boiling point and quantified separately using the CSRF of the corresponding isomer.

For isomers, which have the same boiling point but elute in more than one peak, e.g. 2,2,4-trimethyl-1,3-pentanediolmonoisobutyrate, ensure to integrate the peaks in the calibration in the same way as the peaks in the sample. Quantification can be done in two ways.

1) Integrate all peaks of the isomeric mixture together.

2) Integrate and quantify the isomeric peaks separately. Use the average of the quantification results for the final result of the isomeric compound (not the sum).

9.2 Classification of compounds

In order to determine the VOC and/or SVOC content, the compounds analysed shall be classified to the category VOC or SVOC according to the following priority list (see also Figure 4).

- Identified compounds shall be classified according to requirements as given by the contractor, i.e. any valid legislation, label or a classification.
- If the classification shall be done via the boiling point (BP) of an identified compound, the boiling point shall be taken from the non-exhaustive list of VOC, SVOC and NVOC compounds available in Annex A.
- If an identified substance is not present in this list, a reliable source should be used for referencing the boiling point. This source shall be referenced in the test report.

  NOTE Examples of reliable sources are the disseminated data of the REACH registration on the ECHA website www.echa.europa.eu or the website www.chemspider.com from the Royal Society of Chemistry.

- If no requirement for VOC or SVOC definition is given for identified compounds, the identified compounds should be listed individually.
- If the compounds cannot be identified via their mass spectra, classification can be made by using specific markers (classification by retention time).
- If the compounds cannot be identified via their mass spectra and no boiling point requirement is given, all compounds eluting with a retention time prior or equal to DEA shall be handled as VOC, and all compounds eluting after DEA and prior or equal to C22 shall be handled as SVOC. All compounds eluting after C22 shall be handled as NVOC.

The relative retention time order of substances does not necessarily correlate with boiling point order. Therefore, classification to VOC or SVOC via the use of marker compounds is prone to misclassification. Classification by boiling point or other pre-given requirements is preferred with respect to classification by marker compounds.

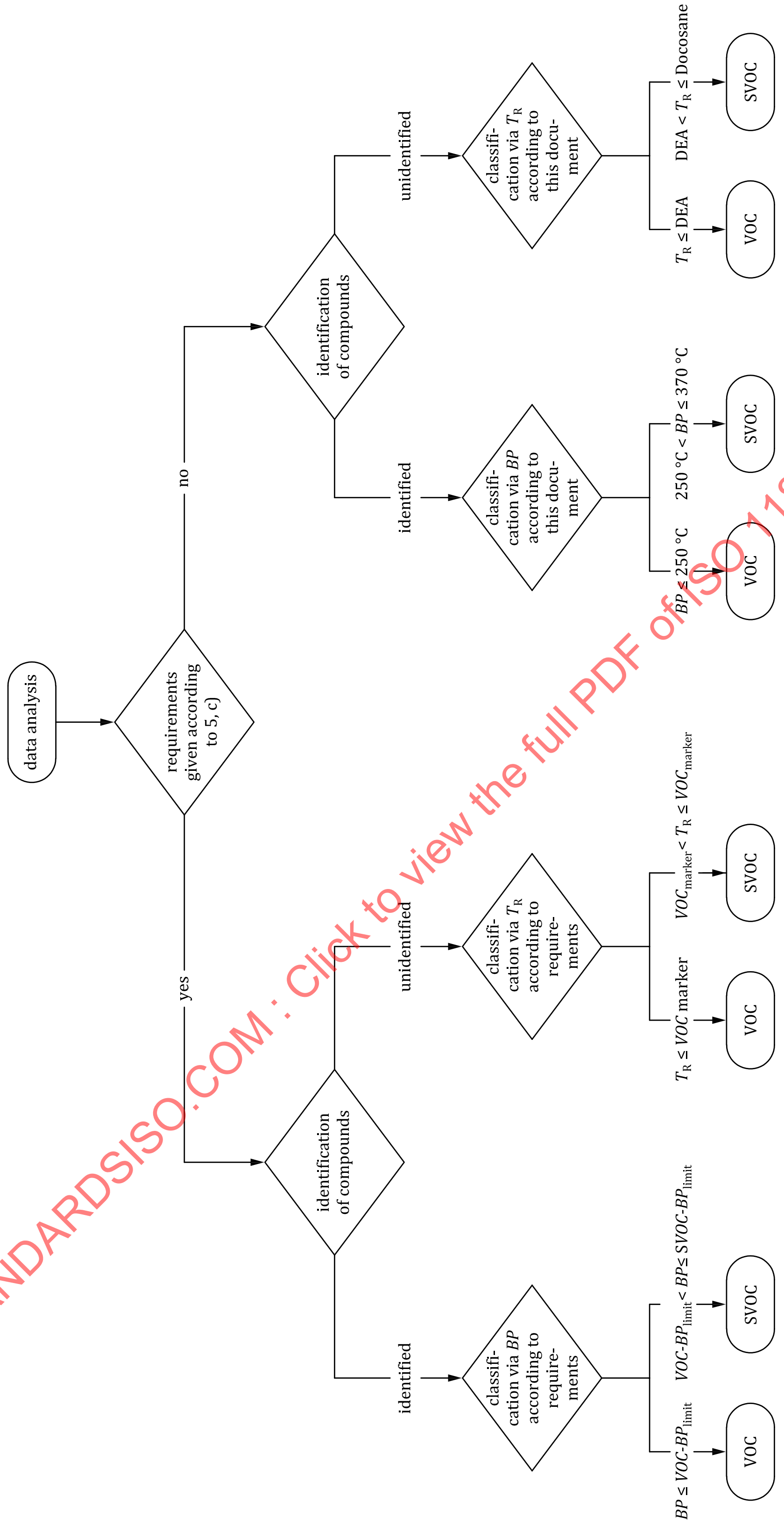


Figure 4 — Scheme for classification of compounds

10 Quantitative determination of compound content

10.1 General

All peaks shall be quantified with an FID detector.

Major peaks shall be quantified using the CSRF, where compounds are commercially available.

All peaks < 0,1 % in DEA equivalents and all peaks ≥ 0,1 % in DEA equivalents classified as non-significant shall be quantified using the calibration with respect to the relative response factor of

a) the surrogate standard (DEA) as specified in 7.3, or

b) a representative compound, i.e. a structural isomer or homologue, as specified in 9.1., or

c) the compound itself (CSRF), when the compound has been identified and calibration data are available, according to 10.2.1.

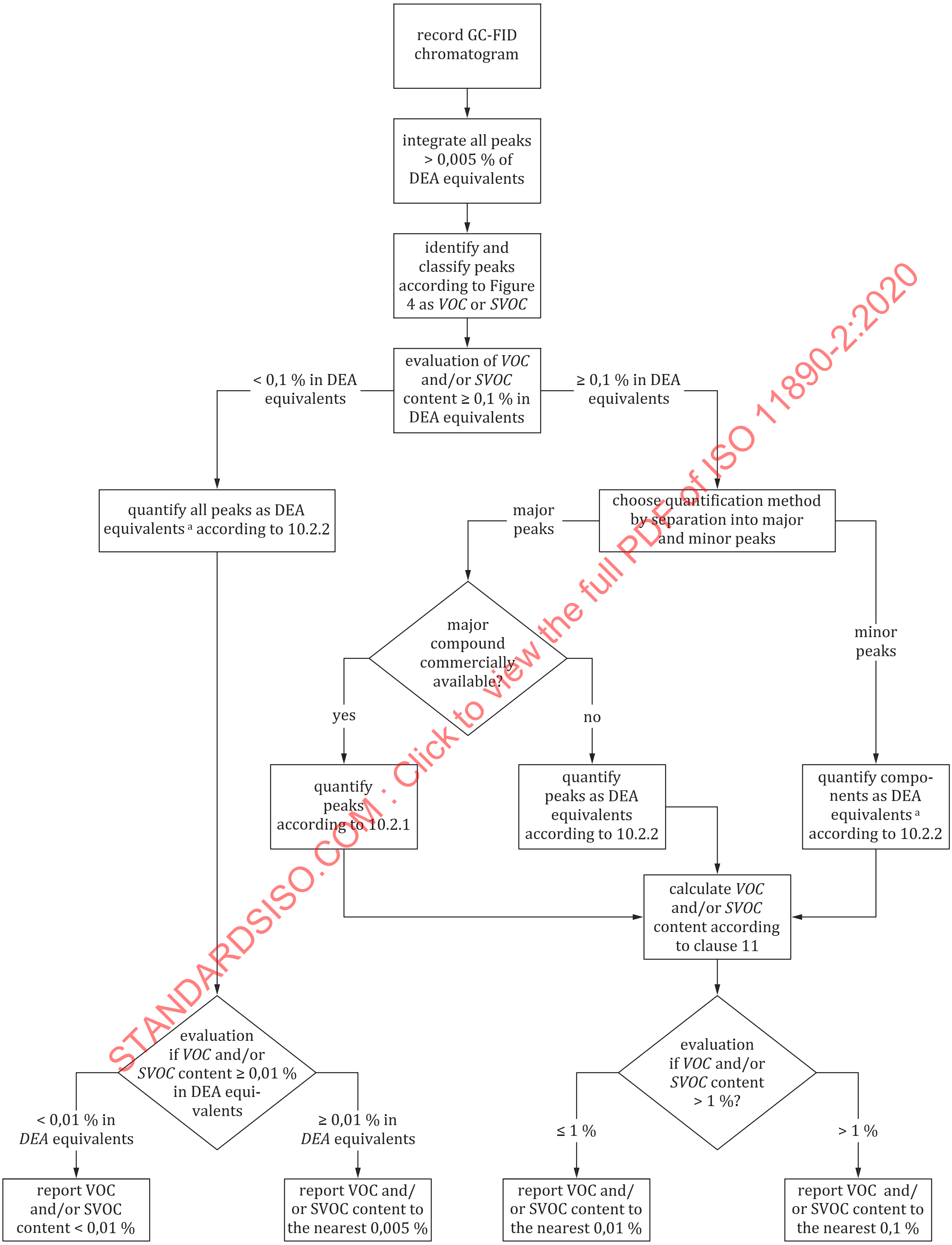
Unidentified peaks are quantified in DEA equivalents.

If the (expected) VOC and/or SVOC content is < 0,1 %, a simplified quantification method can be performed as described in Figure 5. Quantification of VOC and/or SVOC content can be performed with respect to the surrogate standard in the range between 0,01 % by mass and 0,1 % by mass.

NOTE Quantification by CSRF can still be used.

In the calculation of VOC and/or SVOC content, all individual compounds with concentrations equal to or larger than 0,005 % by mass with respect to DEA equivalents shall be considered. If the VOC and/or SVOC content is smaller than 0,01 % by mass report VOC and/or SVOC content “<0,01 % by mass”.

Follow the scheme for quantification as given in Figure 5.



[a] Quantification with respect to CSRF (according to 10.2.1) or another representative compound (as described in 9.1) is possible.

Figure 5 — Quantification scheme

10.2 Quantitative determination of compound content

10.2.1 Quantification with respect to CSRF

Determine the weight fraction of all such compounds of the product using Formula (4):

$$f_i = \frac{r_i \times A_i \times m_{\text{is}}}{m_\text{s} \times A_{\text{is}}} \times 100\ \% \tag{4}$$

where

f_i is the weight fraction of compound *i* in % of the product;

r_i is the CSRF for compound *i* (see 8.3.3);

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 8.2.1);

m_s is the mass, in grams, of the test sample (see 8.2.1).

10.2.2 Quantification with respect to surrogate standard

Determine the weight fraction of all such compounds of the product using Formula (5):

$$f_i = \frac{A_i \times m_{\text{DEA}}}{m_\text{s} \times A_{\text{DEA}}} \times 100\ \% \tag{5}$$

where

f_i is the weight fraction of compound *i* in % of the product;

A_i is the peak area of compound *i*;

A_{DEA} is the peak area of the surrogate standard;

m_{DEA} is the mass, in grams, of surrogate standard in the test sample (see 8.2.1);

m_s is the mass, in grams, of the test sample (see 8.2.1).

11 Calculation of VOC and SVOC content

11.1 General

Calculate the VOC and SVOC content by the method specified in the referring specification. If no particular method is specified, calculate the VOC and SVOC content by method 1, see 11.2.

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).

11.2 Method 1 — VOC content and/or SVOC content, as a percentage by mass, of the product “ready for use”

Apply Formula (6) to VOC determination and Formula (7) to SVOC determination.

$$VOC_{\mathrm{M1}} = \sum_{i=1}^{i=n} f_{i,\mathrm{VOC}} \tag{6}$$

where

VOC_{M1}	is the VOC content, as a percentage by mass, of the product “ready for use”;
$f_{i,\mathrm{VOC}}$	is the weight fraction of compound *i* in % of the test sample (see 10.2).

$$SVOC_{\mathrm{M1}} = \sum_{i=1}^{i=n} f_{\mathrm{i,SVOC}} \tag{7}$$

where

$SVOC_{\mathrm{M1}}$	is the SVOC content, as a percentage by mass, of the product “ready for use”;
$f_{i,\,\mathrm{SVOC}}$	is the weight fraction of compound *i* in % of the test sample (see 10.2).

11.3 Method 2 — VOC content and/or SVOC content, in grams per litre, of the product “ready for use”

Apply Formula (8) to VOC determination and Formula (9) to SVOC determination.

$$VOC_{\mathrm{M2}} = \sum_{i=1}^{i=n} f_{i,\mathrm{VOC}} \times \rho_{\mathrm{s}} \times 10 \tag{8}$$

where

VOC_{M2}	is the VOC content, in grams per litre, of the product “ready for use”;
$f_{i,\mathrm{VOC}}$	is the weight fraction of compound *i* in % of the test sample (see 10.2);
ρ_{s}	is the density, in grams per millilitre, of the test sample at 23 °C (see 8.6);
10	is a conversion factor to convert grams per millilitre in grams per litre.

$$SVOC_{\mathrm{M2}} = \sum_{i=1}^{i=n} f_{\mathrm{i,SVOC}} \times \rho_{\mathrm{s}} \times 10 \tag{9}$$

where

$SVOC_{\mathrm{M2}}$	is the SVOC content, in grams per litre, of the product “ready for use”;
$f_{\mathrm{i,SVOC}}$	is the weight fraction of compound *i* in % of the test sample (see 10.2);
ρ_{s}	is the density, in grams per millilitre, of the test sample at 23 °C (see 8.6);
10	is a conversion factor to convert grams per millilitre in grams per litre.

11.4 Method 3 — VOC content and/or SVOC content, in grams per litre, of the product “ready for use” less water

Apply Formula (10) to VOC content determination.

$$VOC_{\mathrm{M3,lw}} = \left(\frac{\sum_{i=1}^{i=n} f_{i,\mathrm{VOC}}}{100 - \rho_{\mathrm{s}} \times \frac{f_{\mathrm{w}}}{\rho_{\mathrm{w}}}} \right) \times \rho_{\mathrm{s}} \times 1\,000 \tag{10}$$

where

$\mathrm{VOC}_{\mathrm{M3,lw}}$	is the VOC content, in grams per litre, of the product “ready for use” less water;
$f_{i,\mathrm{VOC}}$	is the weight fraction of compound *i* in % of the test sample (see 10.2);
f_{w}	is the weight fraction of water in % of the test sample (see 8.7);
ρ_{s}	is the density, in grams per millilitre, of the test sample at 23° C (see 8.6);
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 to convert grams per millilitre in grams per litre.

Apply Formula (11) to SVOC content determination.

$$SVOC_{\mathrm{M3,lw}} = \left(\frac{\sum_{i=1}^{i=n} f_{i,\mathrm{SVOC}}}{100 - \rho_{\mathrm{s}} \times \frac{f_{\mathrm{w}}}{\rho_{\mathrm{w}}}} \right) \times \rho_{\mathrm{s}} \times 1\,000 \tag{11}$$

where

$\mathrm{SVOC}_{\mathrm{M3,lw}}$	is the SVOC content, in grams per litre, of the product “ready for use” less water;
$f_{i,\mathrm{SVOC}}$	is the weight fraction of compound *i* in % of the test sample (see 10.2);
f_{w}	is the weight fraction of water in % of the test sample (see 8.7);
ρ_{s}	is the density, in grams per millilitre, of the test sample at 23° C (see 8.6);
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 to convert grams per millilitre in grams per litre.

11.5 Method 4 — VOC content and/or SVOC content, in grams per litre, of the product “ready for use” less water and less exempt compounds

This is only required if national legislation applies.

Apply Formula (12) to VOC content determination and Formula (13) to SVOC content determination.

$$VOC_{\mathrm{M4,lwe}} = \left(\frac{\sum_{i=1}^{i=n} f_{i,\mathrm{VOC}}}{100 - \rho_{\mathrm{s}} \times \frac{f_{\mathrm{w}}}{\rho_{\mathrm{w}}} - \rho_{\mathrm{s}} \times \sum_{\mathrm{eci}=1}^{\mathrm{eci}=n} \frac{f_{\mathrm{eci}}}{\rho_{\mathrm{eci}}}} \right) \times \rho_{\mathrm{s}} \times 1\,000 \tag{12}$$

where

$\mathrm{VOC}_{\mathrm{M4,\,lwe}}$ is the VOC content, in grams per litre, of the product “ready for use” less water and less exempt compounds;

$f_{i,\mathrm{VOC}}$ is the weight fraction of compound *i* in % of the test sample (see 10.2);

$f_{\mathrm{e}ci}$ is the weight fraction of exempt compound *i* in % of the test sample (see 10.2);

f_{w} is the weight fraction of water in % of the test sample (see 8.7);

ρ_{s} is the density, in grams per millilitre, of the test sample at 23 °C (see 8.6);

ρ_{w} is the density, in grams per millilitre, of water at 23 °C (= 0,997 537 g/ml);

$\rho_{\mathrm{e}ci}$ is the density, in grams per millilitre, of exempt compound *i*;

1 000 is a conversion factor to convert grams per millilitre in grams per litre.

$$SVOC_{\mathrm{M4,lwe}} = \left(\frac{\sum_{i=1}^{i=n} f_{i,\mathrm{SVOC}}}{100 - \rho_{\mathrm{s}} \times \frac{f_{\mathrm{w}}}{\rho_{\mathrm{w}}} - \rho_{\mathrm{s}} \times \sum_{\mathrm{e}ci=1}^{\mathrm{e}ci=n} \frac{f_{\mathrm{e}ci}}{\rho_{\mathrm{e}ci}}} \right) \times \rho_{\mathrm{s}} \times 1\,000 \tag{13}$$

where

$\mathrm{SVOC}_{\mathrm{M4,lwe}}$ is the SVOC content, in grams per litre, of the product “ready for use” less water and less exempt compounds;

$f_{i,\mathrm{SVOC}}$ is the weight fraction of compound *i* in % of the test sample (see 10.2);

$f_{\mathrm{e}ci}$ is the weight fraction of exempt compound *i* in % of the test sample (see 10.2);

f_{w} is the weight fraction of water in % of the test sample (see 8.7);

ρ_{s} is the density, in grams per millilitre, of the test sample at 23 °C (see 8.6);

ρ_{w} is the density, in grams per millilitre, of water at 23 °C (= 0,997 537 g/ml);

$\rho_{\mathrm{e}ci}$ is the density, in grams per millilitre, of exempt compound *i*;

1 000 is a conversion factor to convert grams per millilitre in grams per litre.

12 Data evaluation and calculation of final results

If two results from duplicate determination differ by more than the repeatability limit *r* from each other, 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 and larger than or equal to 0,1 % by mass, report the result to the nearest 0,01 %. For values < 0,1 % by mass report to the nearest 0,005 % by mass.

13 Precision

13.1 General

The precision of the test method was determined by interlaboratory testing in accordance with ISO 5725-1 and ISO 5725-2. Two different materials were tested by 11 laboratories.

13.2 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, may be expected to be for a probability of 95 %.

The repeatability limit, *r*, for the determination of VOC content and SVOC content is 12 % (relative percentage), as derived from a sixfold repetitive determination of the VOC content and SVOC content in two coating matrices (see Annex D).

NOTE The highest value of the repeatability limit, *r*, determined in the round robin test is used to define the precision data of the method.

13.3 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, may be expected to be for a probability of 95 %.

The reproducibility limit, *R*, for this test method, for the determination of VOC content and SVOC content is 18 % (relative percentage), as derived from round robin test results (see Annex D).

NOTE The highest value of the reproducibility limit, *R*, determined in the round robin test is used to define the precision data of the method.

14 Test report

The test report shall contain at least the following information:

a) a reference to this document, i.e. ISO 11890-2:2020;

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

c) required information according to Clause 5;

d) the results of the test for VOC and SVOC content, as indicated in Clause 10, and the method of calculation used (11.2, 11.3, 11.4 or 11.5);

e) values of repeatability or reproducibility if required by the client or a conformity evaluation is performed;

f) any additional information according to Clause 5 as agreed by the parties;

g) extraction solvent used;

h) any deviation from the test method specified;

i) the date of the test;

j) method of quantification used (CSRF or surrogate standard or combination of both).

Annex A
(normative)

Non-exhaustive list of VOC, SVOC and NVOC compounds

Table A.1 — Non-exhaustive list of VOC, SVOC and NVOC compounds

No.	Substance	CAS-Nr	Boiling range [°C]	No.	Substance	CAS-Nr	Boiling range [°C]
1	3,5,5-Trimethylhexanoic acid	3302–10–1	236	17	2-Ethyl-1-hexanol	104–76–7	184 to 186
2	1,4-Diisopropylbenzene	100–18–5	210,1	18	Cyclohexanedimethanol	105–08–8	285,5
3	Ethylbenzene	100–41–4	136	19	Caprolactam	105–60–2	271
4	Styrene	100–42–5	145	20	Dibutyl fumarate	105–75–9	281
5	Benzylalcohol	100–51–6	205,3	21	Dibutyl maleate	105–76–0	280
6	Benzaldehyde	100–52–7	179	22	Geraniol	106–24–1	229 to 230
7	1-Methyl-3-vinylbenzene	100–80–1	170 to 171	23	p-Xylene	106–42–3	138,4
8	Diphenyl oxide	101–84–8	258	24	1,4-Dichlorobenzene	106–46–7	174
9	Triethanolamine	102–71–6	336,1	25	Dimethyl succinate	106–65–0	196
10	2-Ethylhexyl acetate	103–09–3	199	26	Ethylene glycol	107–21–1	197
11	2-Ethylhexyl acrylate	103–11–7	215	27	Methyl formate	107–31–3	30 to 32
12	Di(2-ethylhexyl)adipate	103–23–1	377,9	28	Hexylene glycol	107–41–5	197
13	2-Phenoxyethyl isobutyrate	103–60–6	275,3	29	1-Methyl-3-propylbenzene	1074–43–7	182
14	n-Propylbenzene	103–65–1	159	30	Butyric acid	107–92–6	164
15	Diethylene glycol monophenylether	104–68–7	296	31	3-Mercaptopropionic acid	107–96–0	210 to 214
16	1-Phenyldecane	104–72–3	293	32	Propylene glycol methyl ether	107–98–2	120
33	Methyl isobutyl ketone	108–10–1	116 to 118	51	n-Hexane	110–54–3	69
34	Isopropyl acetate	108–21–4	87	52	Valeraldehyde	110–62–3	104
35	Maleic anhydride	108–31–6	200	53	1,4-Butanediol	110–63–4	230
36	Propylene carbonat	108–32–7	242 to 243	54	1,2-Dimethoxyethane	110–71–4	85
37	m-Xylene	108–38–3	139,1	55	Ethylene glycol monoethyl ether	110–80–5	136
38	1-Methoxy-2-propyl acetate	108–65–6	146	56	Cyclohexane	110–82–7	81
39	Mesitylene	108–67–8	164,7	57	Diisopropanolamine	110–97–4	248,8 – 254,5
40	Methylcyclohexane	108–87–2	101	58	n-Heptanoic acid	111–14–8	223
41	Toluene	108–88–3	111	59	2-Ethoxyethyl acetate	111–15–9	156
42	Cyclohexanol	108–93–0	160 to 161	60	1-Hexanol	111–27–3	155
43	Cyclohexanone	108–94–1	154	61	Glutaraldehyde	111–30–8	101 to 102

Table A.1 *(continued)*

No.	Substance	CAS-Nr	Boiling range [°C]
44	Phenol	108–95–2	182
45	Valeric acid	109–52–4	184
46	Ethylene glycol isopropylether	109–59–1	145 to 147
47	Ethylene glycol monomethyl ether	109–86–4	124
48	Tetrahydrofuran	109–99–9	65
49	Isobutyl acetate	110–19–0	117
50	2-Methoxyethyl acetate	110–49–6	145
69	Diethylene glycol dimethyl ether	111–96–6	163
70	2-Butoxyethyl acetate	112–07–2	192
71	2-Methylcyclopentanone	1120–72–5	139
72	Ethylene glycol n-hexyl ether	112–25–4	208
73	Triethyleneglycol	112–27–6	286,5
74	1-Decanol	112–30–1	229
75	Decanal	112–31–2	216
76	Diethylene glycol butyl ether	112–34–5	231
77	1-Dodecene	112–41–4	213,8
78	Triethylene glycol dimethyl ether	112–49–2	216
79	Lauryl alcohol	112–53–8	229
80	n-Dodecyl mercaptane	112–55–0	266 to 285
81	Diethylene glycol n-hexyl ether	112–59–4	262
82	1-Bromohexadecane	112–82–3	336
83	Linanyl acetat	115–95–7	220
84	1-Hydroxyacetone	116–09–6	145
85	Cyclopentanone	120–92–3	131
86	Ethyl Vanillin	121–32–4	285 to 294
87	Triethylamine	121–44–8	88 to 90
88	Triisopropanolamine	122–20–3	301
62	Diethanolamine	111–42–2	269,9
63	Diethylene glycol	111–46–6	245
64	Heptanal	111–71–7	156 to 160
65	Ethylene glycol monobutylether	111–76–2	171 to 174
66	1-Octanol	111–87–5	194
67	Diethylene glycol monoethyl ether	111–90–0	196
68	Dimethyl glutarate	1119–40–0	216
90	2-Phenoxyethanol	122–99–6	244 to 246
91	2-Ethylhexanal	123–05–7	160
92	2,6,8-Trimethyl-4-nonanol	123–17–1	225
93	Propanal	123–38–6	48
94	Diacetone alcohol	123–42–2	168
95	Isopentanol	123–51–3	130,7
96	Butanal	123–72–8	75
97	n-Butyl acetate	123–86–4	125 to 126
98	1,4-Dioxane	123–91–1	101 to 102
99	Octanoic acid	124–07–2	237
100	Octanal	124–13–0	175
101	Butyl diglycol acetate	124–17–4	244,9
102	Nonanal	124–19–6	195
103	Isobornyl acetate	125–12–2	225,9
104	Neopentylglycol	126–30–7	209,4
105	Tributyl phosphate	126–73–8	289
106	Tetrachloroethene	127–18–4	121
107	Phosphoric acid, monobutylester	12788–93–1	214 to 218
108	ß-Pinene	127–91–3	166 to 179
109	Butylated Hydroxytoluene	128–37–0	265

Table A.1 *(continued)*

No.	Substance	CAS-Nr	Boiling range [°C]
89	alpha-Amylcinnamic aldehyde	122–40–7	287,2
111	ß-Naphthol	135–19–3	285
112	2-Methylbutanol	137–32–6	128
113	Benzyl acetate	140–11–4	213,5
114	Ethyl acrylate	140–88–5	99,8
115	Diisobutyl adipate	141–04–8	293
116	n-Butyl acrylate	141–32–2	147
117	n-Hexanoic acid	142–62–1	203
118	n-Heptane	142–82–5	98
119	1-Bromododecane	143–15–7	276
120	Triethylen glycol monobutyl ether	143–22–6	278
121	2,2,4-Trimethyl-1,3-pentanediol	144–19–4	228
122	2-Ethylhexanoic acid	149–57–5	226 to 229
123	4-Methoxyphenol	150–76–5	242,8
124	Citronellyl acetate	150–84–5	239,8
125	1-propoxypropan-2-ol	1569–01–3	149,4
126	Trans-2-Pentenal	1576–87–0	125
143	2-ethyl-2,5-dimethylhexanoic acid	26896–20–8	243 to 253
144	Isotridecylalcohol	27458–92–0	260,8
145	2-Propenoic acid, 2-methyl-, monoester with 1,2-propanediol	27813–02–1	209
146	Ethylene glycol monopropyl ether	2807–30–9	147
147	Ethylene glycol monoisopropyl ether	109–59–1	145
148	Diacetonacrylamide	2873–97–4	310
110	Propylene glycol monooleate	1330–80–9	176
127	1-Propylene glycol 2-methyl ether	1589–47–5	130
128	Hexadecyltrimethoxysilane	16415–12–6	350
129	N-[3-(Trimethoxysilyl)propyl] ethylenediamine	1760–24–3	240
130	Acetoacetoxyethyl methacrylate	21282–97–3	266
131	DL-Camphor	21368–68–3	204
132	Phenyloctane	2189–60–8	261 to 263
133	Vinyl toluene	25013–15–4	170
134	tert-Dodecyl mercaptan	25103–58–6	237,9
135	3-Methoxy-1-butanol	2517–43–3	157
136	Dipropyleneglycol	25265–71–8	227
137	2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate	25265–77–4	255 – 261,5
138	[3-(2,3-epoxypropoxy)propyl]-trimethoxysilane	2530–83–8	233,3
139	Tripropylene glycol monomethylether	25498–49–1	242,8
140	5-Chloro-2-methyl-2H-isothiazol-3-one (CMIT)	26172–55–4	200
141	2-Methyl-4-isothiazolin-3-one (MIT)	2682–20–4	182,8
142	N-Ethyl-2-pyrrolidone	2687–91–4	212,5
163	Citral	5392–40–5	230
164	Dodecamethylcyclohexasiloxane (D6)	540–97–6	245
165	Decamethylcyclopentasiloxane (D5)	541–02–6	210
166	Octamethylcyclotetrasiloxane (D4)	556–67–2	175
167	Tripropylene glycol n-butylether	55934–93–5	275
168	Tetrachloromethane	56–23–5	76,8

Table A.1 *(continued)*

No.	Substance	CAS-Nr	Boiling range [°C]
149	Alkyltriethoxysilane	2943–75–1	259,6
150	Dipropylene glycol n-propyl ether	29911–27–1	212
151	Dipropylene glycolbutylether	29911–28–2	230
152	Diisononyladipate	33703–08–1	232 to 233
153	2-(Hydroxymethylamino)ethanol	34375–28–5	110
154	Dipropylene glycol monomethyl ether	34590–94–8	189,6
155	1-Hexadecanol	36653–82–4	319
156	Crotonaldehyde	4170–30–3	102,2
157	4-Phenylcyclohexene	4994–16–5	243
158	Formaldehyde	50–00–0	99,4
159	Vinyl neodecanoate	51000–52–3	212
160	Propylene glycol n-butyl ether	5131–66–8	171
161	1,2,3-Trimethylbenzene	526–73–8	175 to 176
162	Phenyl acetylene	536–74–3	142 to 144
183	Dimethyl adipate	627–93–0	230,9
184	1,2-Diethoxyethane	629–14–1	119,4
185	1-Hexadecene [Cetene]	629–73–2	284,9
186	ß-Methylstyrene	637–50–3	172 to 173
187	Acetic acid	64–19–7	117,9
188	Benzoic acid	65–85–0	249,2
189	Acetone	67–64–1	56,1
190	Dimethylformamide	68–12–2	152 to 153
191	(3-Aminopropyl)silanetriol	68400–07–7	297,6
192	2,2,4-Trimethyl-1,3- pentanedioldiiso-butyrate	6846–50–0	281
193	1-Butanol	71–36–3	119
194	1-Pentanol	71–41–0	138
195	Butyl glycolate	7397–62–8	180
169	3-Methyl-2-butanone	563–80–4	94,2
170	Glycerol	56–81–5	290
171	Stearic acid	57–11–4	361
172	Propylene glycol	57–55–6	184
173	2-Methylcyclohexanone	583–60–8	162 to 163
174	3-Pentanol	584–02–1	114 to 115
175	Butyl formate	592–84–7	106 to 107
176	2-Methyl-3-butanol	598–75–4	112
177	L-Limonene	5989–54–8	176
178	2-Pentanol	6032–29–7	118 to 119
179	2-Ethyltoluene	611–14–3	164 to 165
180	1-Methyl-2-vinylbenzene	611–15–4	170 to 172
181	Propylene glycol diacetate	623–84–7	191,5
182	Hexyl salicate	6259–76–3	297,6
201	Camphor	76–22–2	204
202	1,2-Propylene glycol dimethyl ether	7778–85–0	96
203	Trimethylolpropane	77–99–6	304,2
204	Triethyl phosphate	78–40–0	216
205	Isobutanol	78–83–1	108
206	2-Butanone [MEK]	78–93–3	79,6
207	Propionic acid	79–09–4	140,7 to 141,4
208	Isobutyric acid	79–31–2	156
209	Methacrylamid	79–39–0	225
210	Citronellal	8000–29–1	206 to 208
211	α-Pinene	80–56–8	approx. 154,3
212	Methyl methacrylate	80–62–6	100,4
213	Phthalic anhydride	85–44–9	284,5

Table A.1 *(continued)*

No.	Substance	CAS-Nr	Boiling range [°C]	No.	Substance	CAS-Nr	Boiling range [°C]
196	Acetaldehyde	75–07–0	20,2	214	2-Hydroxyethyl methacrylate	868–77–9	213
197	tert-Butanol	75–65–0	82,4	215	N-Methyl-2-pyrrolidone	872–50–4	204
198	2,2-Dimethyl-1-propanol	75–84–3	113 to 114	216	Camphor	76–22–2	204
199	2-Methyl-2-butanol	75–85–4	102,4	217	o-Phenylphenol	90–43–7	287
200	Pivalic acid	75–98–9	160 to 162	218	Naphthalene	91–20–3	218,1
219	Coumarin	91–64–5	301,7	232	α-Methylstyrene	98–83–9	165,4
220	(3-aminopropyl)triethoxysilane	919–30–2	217	233	Acetophenone	98–86–2	202,1
221	Diisobutyl Succinate	925–06–4	252	234	1,3-Diisopropylbenzene	99–62–7	203
222	Indene	95–13–6	181 to 182	235	Camphor	76–22–2	204
223	o-Xylene	95–47–6	144,5	236	n-Docosane	629–97–0	365
224	1,2,4-Trimethylbenzene	95–63–6	169	237	Dibutylsebacate	109–43–3	344,5
225	1,2,4,5-Tetramethylbenzene	95–93–2	191 to 193	238	n-Tetradecane	629–59–4	252 to 266
226	2-Butanonoxime	96–29–7	152	239	Triethylene glycol	112–27–6	286,5
227	Methyl acrylate	96–33–3	80,1	240	Diethyladipate	141–28–6	246,7 to 252
228	Butyrolactone	96–48–0	204,6	241	Acetonitrile	75–05–8	81,6
229	Ethylene carbonate	96–49–1	247	242	Methanol	67–56–1	64,7
230	Furfural	98–01–1	162	243	Tetrahydrofuran	109–99–9	65
231	Isopropylbenzene	98–82–8	152,4				

Annex B
(informative)

Information on thermal unstable products

B.1 Occurrence of thermal degradation of matrices by the analytical methods from Clause 8

The purpose of this annex is to provide information and guidance.

Tests with different classes of polymer dispersions have shown that, when using the prescribed injection temperature of 250 °C, unexpected peaks can occur in the chromatograms, when thermally unstable products or substances are present in the tested material. Examples of thermal unstable polymers and components are:

a) polyurethanes, which thermally degrade from temperatures as low as 150 °C;

b) poly-acrylates/ poly-methacrylates, which thermally degrade at temperatures around 200 °C;

c) poly-dimethylsiloxanes;

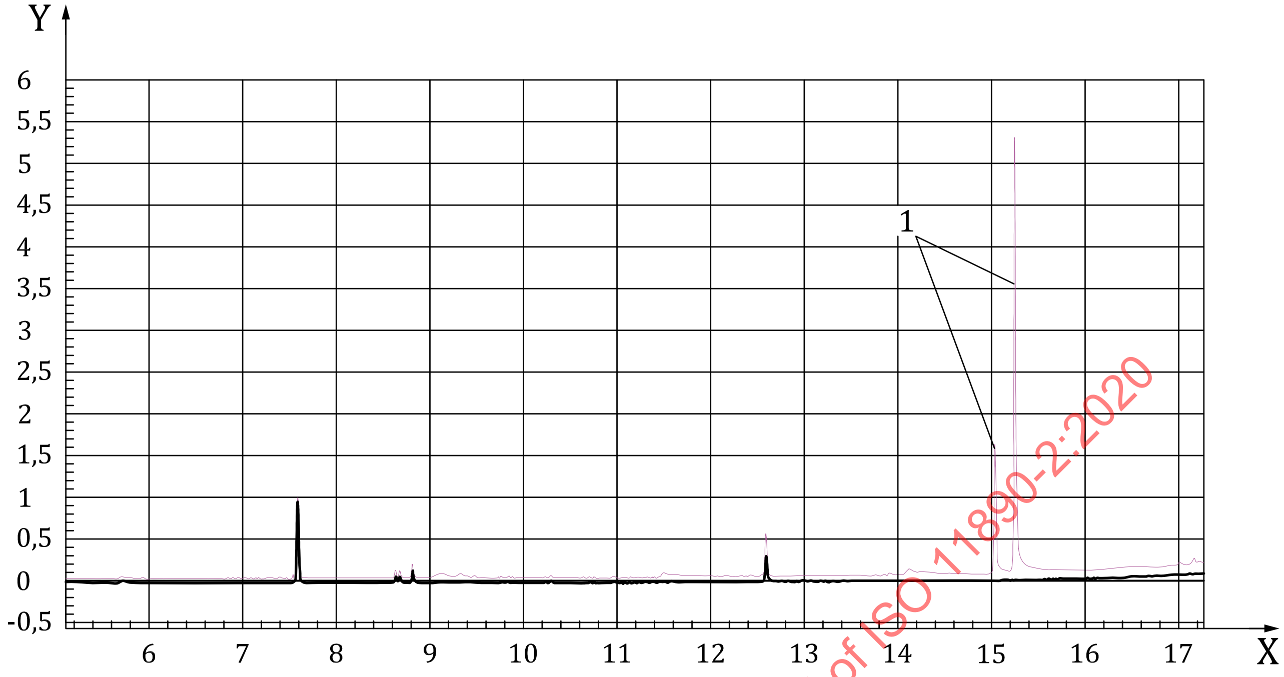
d) emulsifiers, e.g. sodium dodecyl sulfate which splits off dodecanol.

When analysing these kinds of polymers, be aware that degradation signals can occur in the chromatogram. This can be checked by looking for changes in the chromatogram when injecting the sample at various injector temperatures. Identified degradation peaks shall not be included in the calculation of the VOC and/or SVOC content.

The examples B.2 to B.5 show the influence of the injector temperature on the formation of decomposition products. As a general rule, the higher the injection temperature, the more decomposition products are formed.

B.2 Example 1 — Polyurethane dispersion

The polyurethane dispersion in this example contains no free isocyanates (NCO). From Figure B.1, it can be seen that with an increased temperature NCO signals appear in the chromatogram. So the presence of NCO signals in the chromatogram of a polyurethane dispersion, injected at 250 °C, is a strong indication that thermal degradation occurred.



Key

X retention time in minutes

Y signal in millivolt

1 NCO

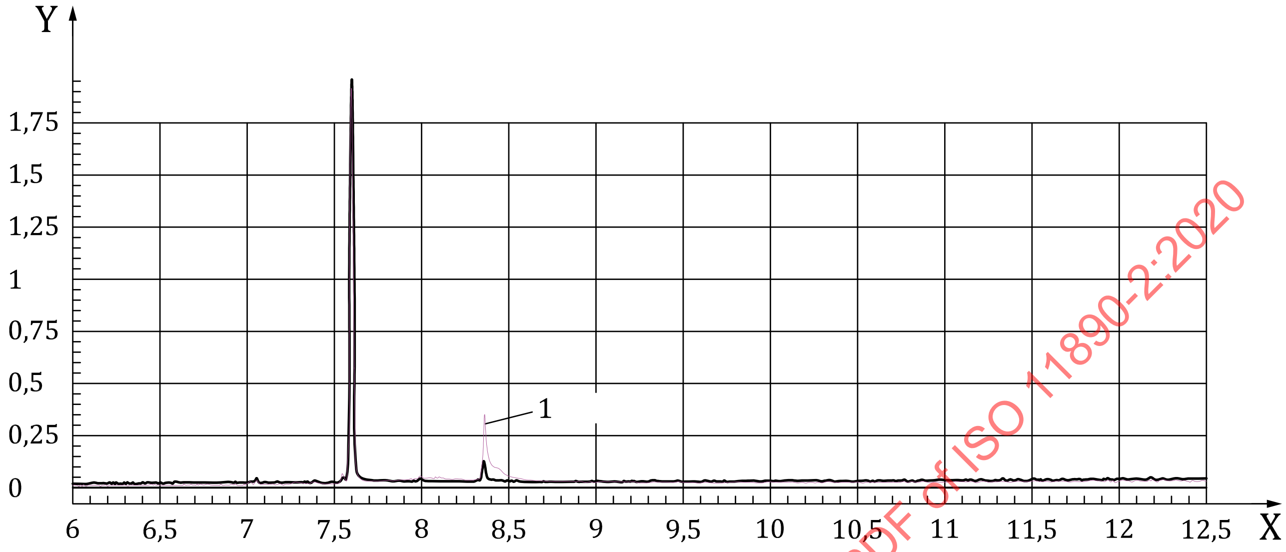
Figure B.1 — Overlay chromatogram of a poly urethane dispersion injected at 160 °C (black) and 250 °C (pink)

Chromatographic conditions used in example 1

Injector temperatures used:	160 and 250 °C
Split ratio:	1:50
Injection volume:	1,0 µl, automatic injection
Oven temperature programme:	initial temperature: 40 °C
	isothermal holding time: 1 min
	heating rate: 15 °C/min
	final temperature: 300 °C
	isothermal holding time: 12 min
Detector temperature:	320 °C
Carrier gas:	Helium
	column inlet pressure: 222,4 kPa
	linear flow rate through column: 38,7 cm/s
Column:	length: 60 m
(HP-5 MS UI)	internal diameter: 0,25 mm

B.3 Example 2 — Poly-methacrylate

The backbone of the poly-methacrylate in this example contained among others butyl methacrylate (BMA). From Figure B.2, it can be seen that the intensity of the BMA signal increased with an increased injection temperature, which is caused by degradation of the backbone of the polymer.



Key

X	retention time in minutes
Y	signal in millivolt
1	BMA

Figure B.2 — Overlay chromatogram of a poly-methacrylate injected at 175 °C (black) and 250 °C (pink)

Chromatographic conditions used in example 2

Injector temperatures used:	170 and 250 °C
Split ratio:	1:50
Injection volume:	1,0 µl, automatic injection
Oven temperature programme:	initial temperature: 40 °C
	isothermal holding time: 1 min
	heating rate: 15 °C/min
	final temperature: 300 °C
	isothermal holding time: 12 min
Detector temperature:	320 °C
Carrier gas:	Helium
	column inlet pressure: 222,4 kPa
	linear flow rate through column: 38,7 cm/s