TECHNICAL SPECIFICATION

ISO/TS 17796

First edition
2013-06-15

Rubber — Trapping and identification of volatile components of rubber fumes with active sampling on a poly(2,6-diphenylphenylene oxide) type sorbent, using thermodesorption and gas chromatographic method with mass spectrometric detection

Caoutchouc — Piégeage et identification des composés volatils des fumées de procédés du caoutchouc, par échantillonnage actif sur un sorbant de type poly(oxyde de 2,6-diphénylphénylène), en utilisant une méthode par thermodésorption et chromatographie en phase gazeuse avec détection par spectrométrie de masse

Reference number
ISO/TS 17796:2013(E)

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

Published in Switzerland

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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.

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The committee responsible for this document is ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

Rubber — Trapping and identification of volatile components of rubber fumes with active sampling on a poly(2,6-diphenylphenylene oxide) type sorbent, using thermodesorption and gas chromatographic method with mass spectrometric detection

1 Scope

This Technical Specification specifies a qualitative method of thermodesorption – gas chromatography – mass spectrometry (TD-GC-MS) for the identification of volatile components in rubber fumes, after trapping on a solid sorbent based on 2,6-diphenylphenylene-oxide polymer resin. It is applicable to a screening of emissions from the processing of rubber compounds in the ambient workplace and storage environment.

CAUTION — Persons using this Technical Specification should be familiar with the procedures for gas chromatography – mass spectrometry measurement and analysis. All the operative details for the application and set-up of the GC-MS are assumed to be in agreement with the operative instructions provided by the manufacturer. Therefore, the detailed procedure for the operation is not included in this Technical Specification. This Technical Specification specifies a qualitative method which is not aimed at quantitative analyses.

2 Terms and definitions

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

2.1
semi-volatile organic compound
SVOC
organic compound whose boiling point is in the range from (240 to 260) °C to (380 to 400) °C

Note 1 to entry: This classification has been defined by the World Health Organization.[4]

Note 2 to entry: Boiling points of some compounds are difficult or impossible to determine because they decompose before they boil at atmospheric pressure. Vapour pressure is another criterion for the classification of compound volatility that may be used for the classification of organic chemicals. SVOCs have vapour pressures of between 10^{-2} kPa and 10^{-8} kPa.

2.2
volatile organic compound
VOC
organic compound whose boiling point is in the range from (50 to 100) °C to (240 to 260) °C

Note 1 to entry: This classification has been defined by the World Health Organization.[4]

Note 2 to entry: Boiling points of some compounds are difficult or impossible to determine because they decompose before they boil at atmospheric pressure. Vapour pressure is another criterion for the classification of compound volatility that may be used for the classification of organic chemicals. VOCs generally have saturation vapour pressures at 25 °C greater than 10^2 kPa.

2.3
very volatile organic compound
VVOC
organic compound whose boiling point is in the range from <0 °C to (50 to 100) °C

Note 1 to entry: This classification has been defined by the World Health Organization.[4]

Note 2 to entry: Boiling points of some compounds are difficult or impossible to determine because they decompose before they boil at atmospheric pressure. Vapour pressure is another criterion for the classification of compound volatility that may be used for the classification of organic chemicals. VVOCs typically have vapour pressures of greater than 15 kPa.

3 Principle

Rubber fumes are sampled on an adsorbent support using a pump. They are recovered from the trap by thermal desorption and the substances composing the desorbed fume are identified by the mass spectrometer. The method identifies the components adsorbed on the trap support used, except benzene.

The actual composition of the emissions depends on the selection of ingredients used for compounding and on the thermal and mechanical conditions applied to the rubber. Moreover, environmental humidity might interfere with the sorption capability of the sorbent material.

The sorbent tube is used for the trapping of volatile (VOC) (boiling point >50 °C to 100 °C) and semi-volatile (SVOC) (boiling point >240 °C) organic compounds in the C6 to C26 range, which are chemically stable against a desorption temperature of 200 °C. Very volatile compounds (VVOC) (boiling point approximately 50 °C to 100 °C) are only partially retained by the sorbent. Other sorbents based on carbon molecular sieve or by multi-sorbent bed tube may be more appropriate in this case.

The upper limit of the useful range is set by the sorptive capacity of the sorbent used and by the linear dynamic range of the gas chromatograph column and detector or by the sample-splitting capability of the analytical instrumentation used. The sorptive capacity is measured as a breakthrough volume of air, which determines the maximum air volume that shall not be exceeded when sampling.

NOTE Small amounts of benzene could be created by the thermal decomposition of the sorbent.

4 Sampling

4.1 Equipment

4.1.1 Trap support, poly(2,6-diphenylphenylene oxide)[1)], of quantity 180 mg to 200 mg, of particle size 0,18 mm to 0,25 mm (60/80 mesh), and of specific surface 20 m^2/g to 35 m^2/g. Another quantity, particle size or specific surface may be chosen if the test result is proven to be equivalent.

4.1.2 Adsorbent tubes, stainless steel tube.

4.1.3 Calibrated pump

Calibrate the pump with the sorbent tube assembly inline, using a calibrated external flowmeter.

One end of the calibrated flowmeter shall be kept at atmospheric pressure to ensure proper operation.

4.2 Operating conditions

4.2.1 Trap support

Recondition the trap sorbent material before sampling, heating it at 300 °C under inert gas for 1 h (minimum) to 8 h (maximum). Check the cleaning of the trap support by GC-MS analysis.

Recondition tubes stored for more than four weeks before sampling.

1) One example of poly(2,6-diphenylphenylene oxide) is Tenax TA®, which is an example of a suitable product available commercially. This information is given for the convenience of users of this Technical Specification and does not constitute an endorsement by ISO of this product.

4.2.2 Sampling flowrate

The sampling flowrate shall be 100 ml/min maximum at room temperature.

4.2.3 Sampling volume

The sampling volume shall be 6 l maximum.

Two sampling tubes should be placed in parallel, in the same location, and operated simultaneously in case of trap or analysis dysfunction. Only one tube shall be analysed.

4.3 Procedure

When used for fixed-location sampling, a suitable sampling site is to be chosen. The location of sampling shall be close to the source. Sampling the surrounding atmosphere is also admissible.

Assemble the sampling line. The sampling train includes, in the following order, a sample source, a sampling tube(s), a flow controller and a pump. Prepare a tube assembly by joining the tubes in series with a union if more than one tube is used to ensure that the breakthrough volume for the analyte of interest is not exceeded. Attach the pump to the sorbent tube or tube assembly with plastic (PE or PTFE) or rubber tubing. Turn on the pump and adjust the flowrate so that the recommended sample volume is taken within the available time. The recommended air sample volume for the VOCs covered by this Technical Specification amounts to a total of 6 l maximum. An appropriate sampling flowrate is in the range of 50 ml/min to 100 ml/min. Note the starting time, temperature and, if necessary for calculation, also the barometric pressure. At the end of the sampling period, note the flowrate or register the readings. Turn off the pump, and note the time, temperature and, if necessary, barometric pressure. Disconnect the sampling tube from the sampling line and seal both ends using screw-cap fittings with PTFE ferrules.

If the sampling flowrate is determined by using an integrated flow-measuring device, e.g. a mass flowmeter, connect the sampling tube to the sampling line, start the pump, note the time and flowrate or register readings. Note temperature and, if necessary, barometric pressure. An appropriate sampling flowrate is in the range of 50 ml/min to 100 ml/min. At the end of the sampling period, note the flowrate or register readings. Turn off the pump, note and register the time the pump was turned off. Disconnect the sampling tube from the sampling line and seal both ends using screw-cap fittings with PTFE ferrules.

For storage between sampling and analyses, store the closed tubes at room temperature in a container free of any emission. The storage time shall not exceed four weeks.

5 Thermal desorption, gas chromatography – mass spectrometry

5.1 General

For analysis, volatile compounds are thermally desorbed from the sampling tubes. The individual substances are separated using a capillary column in a gas chromatograph and detected with a mass spectrometric detector.

5.2 Reagents

5.2.1 Trap coolant, used for freezing the cool trap in the thermal desorption apparatus (−30 °C or colder). Liquid nitrogen or other alternatives (e.g. a Peltier device) are required. A secondary sorbent cold trap may be used to focus the analytes.

5.2.2 Gas chromatograph carrier gas, helium.

5.3 Apparatus

5.3.1 Thermal desorption apparatus or equivalent, connectable with a gas chromatograph and capable of heating up to 300 °C.

5.3.2 Gas chromatograph, equipped with the following accessories:

— capillary column;

— stationary phase: 5 % diphenyl, 95 % polydimethylsiloxane;

Experience shows that a column of 60 m, diameter 0,25 µm and 0,20 µm thickness film, with a flowrate of 1,2 ml/min is usually appropriate.

— injector system: depending on the desorption system;

— split value: properly adapted in accordance with the sampled amount;

— oven temperature program: established to separate compounds.

5.3.3 Mass spectrometer, quadrupole mass spectrometer in electronic impact mode, specified as follows:

— transfer line temperature: 300 °C;

— ion source temperature: 230 °C to 300 °C;

— ionizing voltage: 70 eV;

— scan range: 25 m/z to 600 m/z;

— analysis mode: full scan.

5.4 Procedure

5.4.1 Principle

Heat the support at 200 °C and trap the volatile compounds generated during the heating period at a temperature of –30 °C or colder. After desorption and cold trapping to preconcentrate the analytes, start the GC-MS measurement in order to obtain the gas chromatogram and mass spectra.

5.4.2 Thermal desorption

Typical desorption conditions for volatile compounds analysis using a secondary cold trap and sampling tube containing 180 mg to 200 mg of sorbent are:

— desorption temperature: 200 °C;

— desorption time: 30 min;

— desorption gas flowrate: 50 ml/min;

— cold-trap high temperature: 300 °C;

— cold-trap low temperature: –30 °C or colder;

— transfer-line temperature: 250 °C minimum;

— split ratios: split ratios between the sample tube and secondary trap and between the secondary trap and analytical column (if applicable) should be selected depending on the expected atmospheric concentration. (See the handbook of the respective manufacturers of the thermal desorption apparatus.).

5.4.3 Analysis

For the identification of single, non-target substances, analyse the samples in the scan mode. Identify substances detected in the sample using the mass spectrometer's total ion chromatogram and the retention time of the compounds. The identification of substances is achieved by matching the unknown mass spectrum with the reference mass spectrum stored in a library of pure substances. This task is usually performed by specialized algorithms included in the software of the GC-MS equipment. The quality of the match is indicated with a custom match index. The acceptance of the matching result is based on the analyst carrying out visual comparison of the mass spectra.

NOTE As a general indication, a quality index greater than 90 % or a reference standard using retention time and mass spectrum will grant the correct identification of the substance.

Substance identification and acceptance of the proposed mass spectra from library research shall be validated by the operator.

5.4.4 Verification of the system

5.4.4.1 Analysis of laboratory blank

A sorbent sampling tube, conditioned according to 4.2.1, is analysed under the conditions stated in 5.4.3. The resulting chromatogram shall be clean of peaks.

5.4.4.2 Analysis of a control standard

For the qualification of the TD-GC-MS system and its sensitivity, a control standard mix shall be analysed. The mix consists of model substances solved in an appropriate solvent. A sorbent sampling tube shall be spiked with a defined volume by means of a microlitre syringe on the surface of the sorbent material in the tube. After this, a defined volume of pure air shall be pumped through the sampling tube according to the sampling procedure as stated above. The breakthrough volume is to be checked by using a second tube connected downstream of the first. Both tubes shall be analysed according to the procedure in 5.4.

The TD-GC-MS chromatogram has to show all peaks of the control components, and a signal-to-noise ratio of 3 to 1 shall be reached as a minimum.

Considering the determination of some specially selected components, the control mix shall be adjusted to the Scope.

NOTE 1 The substances in Table 1, dissolved in an appropriate solvent, have proved suitable for checking the system.

NOTE 2 The Grob solution is also possible.

Table 1 — Control mixture

Benzene	*n*-Undecane
n-Heptane	2,6-Dimethylphenol
Toluene	*n*-Dodecane
n-Octane	*n*-Tridecane
p-Xylene	*n*-Tetradecane
o-Xylene	Dicyclohexylamine
n-Nonane	*n*-Pentadecane
n-Decane	*n*-Hexadecane
2-Ethylhexanol-1	Di-(2-ethylhexyl) adipate

6 Test report

The test report shall include the following particulars:

a) sample details: sampling conditions (date, location, duration, volume, flowrate, temperature, relative humidity);

b) test method:

- reference to the test method used, i.e. to this Technical Specification (ISO/TS 17796);
- desorption temperature and time, characteristics of the column, thermal programme, split condition, spectral condition;
- identification of the TD-GC-MS equipment used;

c) test details: details of any procedures not specified in this Technical Specification, if any;

d) test results:

- chromatograms of sample, laboratory blank, control standard mix;
- identified substances with CAS registry number and retention time;
- main unidentified substances with retention time, mass spectrum and eventual proposal of empirical formula;

e) date of test.

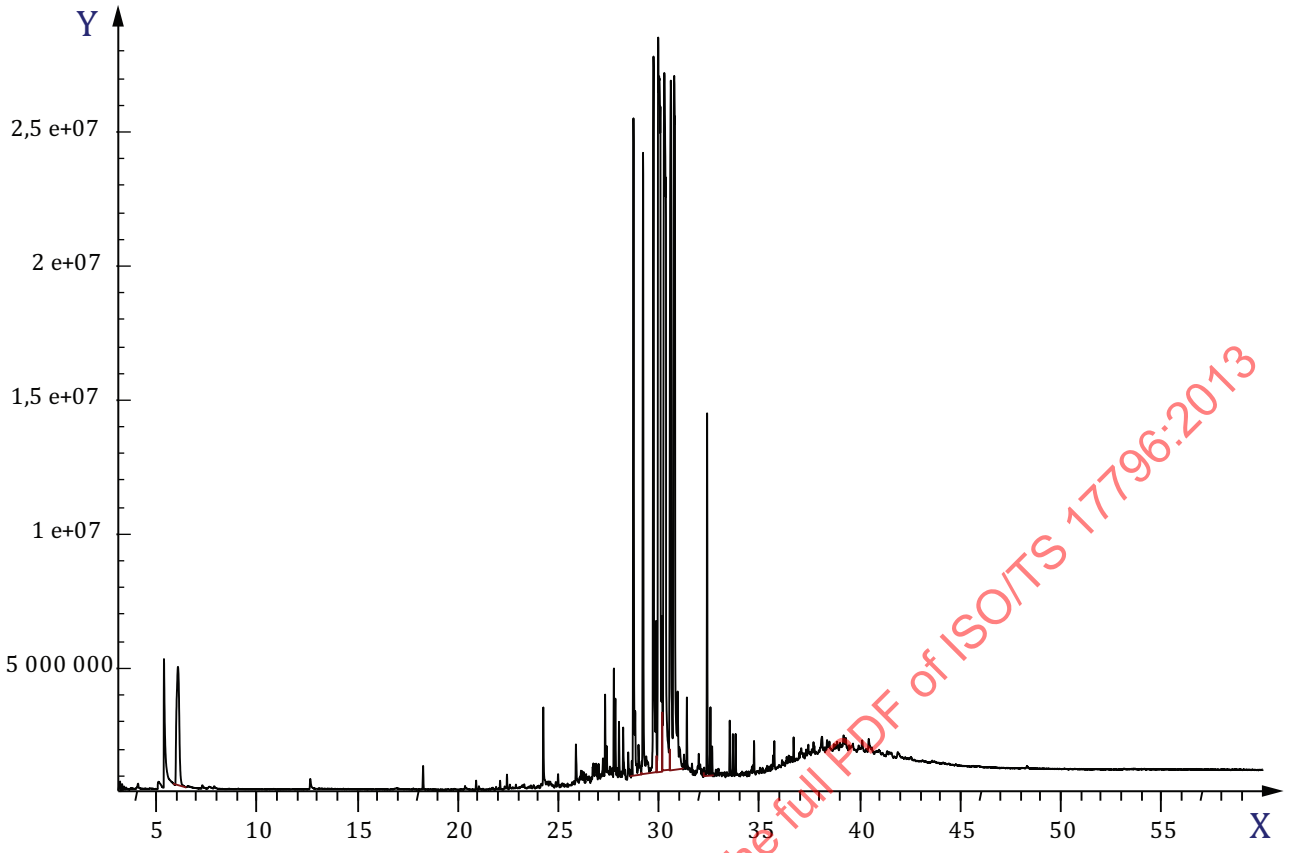
Annex A
(informative)

Example of application to a laboratory EPDM/peroxide mix

See Tables A.1 and A.2; see Figure A.1.

Table A.1 — EPDM/peroxide mixture

EPDM/peroxide mixture	phr
EPDM (Vistalon 2504)	100,00
Carbon black N550	30,00
Kaolin calcinated	20,00
Paraffin oil (Flexon 845)	30,00
ZnO	3,00
Stearic acid	1,50
PEG	1,50
Silica	20,00
Silane	0,50
Bis(tert-butylperoxy isopropyl)benzene (Peroximon F40)	8,00
Triallyl isocyanurate (Diak 7)	1,50
2,2,4-Trimethyl-1H-quinoline (Permanax TQ)	2,00



Key

Y abundance

X time

Figure A.1 — Chromatogram

Table A.2 — Molecules detected in the 1 h sampling of EPDM during curing with peroxide — Thermodesorption 30 min at 300 °C

Retention time (min)	Substance	CAS number
5,08	Ethanol	64–17–5
5,36	Acetone	67–64–1
6,05	2-Propanol, 2-methyl	75–65–0
7,63	Propane, 2-methoxy-2-methyl	1634–04–4
21,13	Octane, 2,6-dimethyl	2051–30–1
22,46	Decane	124–18–5
24,26	Benzenemethanol, α,α-dimethyl-	617–94–7
25,00	2-Cyclohexen-1-one, 3,5,5-trimethyl-	78–59–1
25,46	Undecane, 3-methyl	1002–43–3
25,89	1,2,3-Trimethylindene	4773–83–5
26,13	Undecane, 2,5-dimethyl	17301–22–3

Table A.2 *(continued)*

Retention time (min)	**Substance**	**CAS number**
26,75	Nonane, 5-butyl	17132–63–9
26,83	Dodecane, 4-methyl	6117–97–1
27,02	Dodecane, 3-methyl	17312–57–1
27,34	Benzene, 1,3-bis(1-methylethenyl)	3748–13–8
27,43	Tridecane	629–50–5
27,85	Benzene, 1,4-bis(1-methylethenyl)	1605–18–1
28,03	1,[4-(1-Methylethyl) phenyl]- ethanone	645–13–6
28,24	Benzyl alcohol,α,α-dimethyl-p-isopropyl-	3445–42–9
28,75	1-Isopropyl -ter-butylbenzene	20033–12–9
29,23	1-[4-(1,1-Dimethylethyl) phenyl]- ethanone	943–27–1
29,75	1,1'-(1,4-Phenylene) bis- ethanone	1009–61–6
29,87	Acetophenone, 2'-(trimethylsiloxy)-	33342–85–7
29,97	Phenylene bis- ethanone	
30,29	1-[4-(1-Hydroxy-1-methylethyl)phenyl]- ethanone	54549–72–3
30,60	α,α'-Dihydroxy-m-diisopropylbenzene	1999–85–5
30,78	(Hydroxy methylethyl) phenyl) ethanone	
31,41	Hexadecane	544–76–3
31,99	Pentadecane, 2,6,10-trimethyl	3892–00–0
32,42	Triallyl isocyanurate	1025–15–6
32,59	Heptadecane	629–78–7
32,66	Pentadecane, 2,6,10,14-tetramethyl	1921–70–6
33,70	Octadecane	593–45–3
34,76	Nonadecane	629–92–5

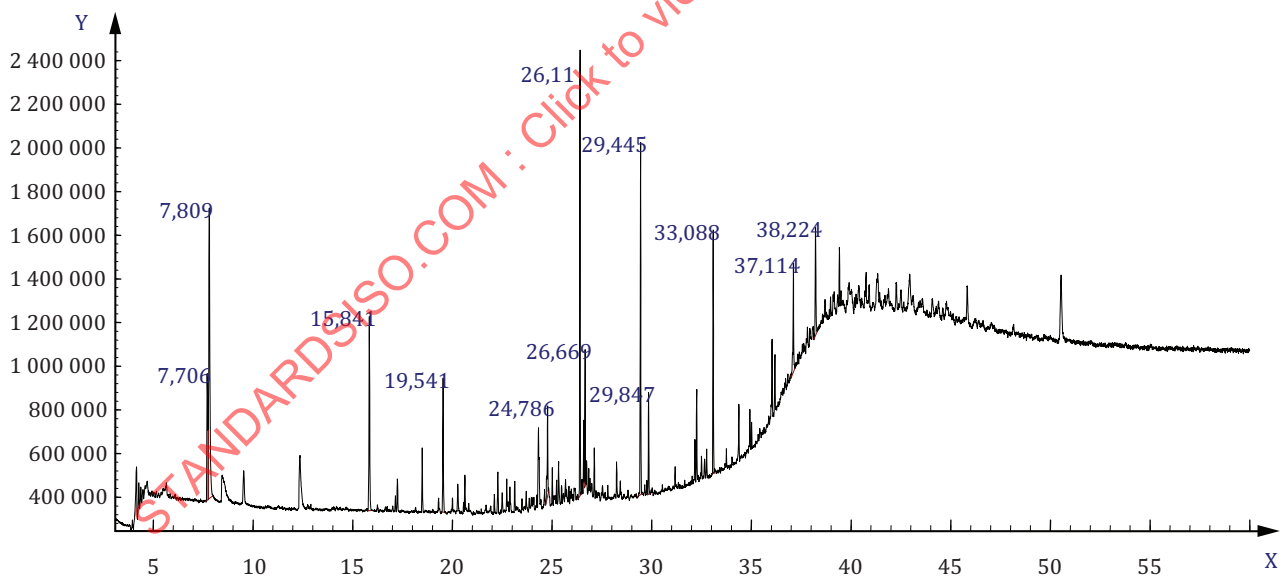
Annex B
(informative)

Example of application to a laboratory NR mix

See Tables B.1 and B.2; see Figure B.1.

Table B.1 — NR mixture

NR mixture	phr
NR - TSR 10CV60	100,00
Carbon black N660	30,00
6PPD	2,00
Paraffin waxes (Antilux 500)	1,00
ZnO	3,00
Stearic acid	2,00
Sulfur	1,00
TBBS	4,00



Key

Y abundance

X time

Figure B.1 — Chromatogram