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Plastics — Poly(vinyl chloride) — Determination of residual vinyl chloride monomer using gas-chromatographic method

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Contents

Page

Foreword ..... **iv**

1 Scope **1**

2 Normative references **1**

3 Terms and definitions **1**

4 Principle **1**

5 Sampling **1**

6 Apparatus **1**

7 Reagents and materials **2**

8 Procedure **3**
8.1 Preparation of test solutions 3
8.2 Gas chromatography 3
8.3 Determination 3
8.4 Preparation of the calibration graph 4

9 Calculation **4**

10 Precision **4**

11 Test report **4**

Annex A (informative) **Suitable GC columns for the determination of vinyl chloride monomer** **6**

Annex B (informative) **Typical responses for vinyl chloride monomer calibration solutions** **7**

Bibliography **8**

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 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties,* in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 249, *Plastics,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This third edition cancels and replaces the second edition (ISO 6401:2008), which has been technically revised.

The main changes are as follows:

— a reference for the density of *N*,*N*′-dimethylacetamide has been added;

— the condition for storing vinyl chloride standard solutions has been specified more precisely;

— the formula for the expression of the vinyl chloride content in relation to the amount of resin has been corrected;

— the test report has been extended.

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.

Plastics — Poly(vinyl chloride) — Determination of residual vinyl chloride monomer using gas-chromatographic method

SAFETY PRECAUTIONS — Persons using this document should be familiar with normal laboratory practice, if applicable. This document does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine applicability of any regulatory requirements.

1 Scope

This document specifies a method for the determination of vinyl chloride monomer in homopolymer and copolymer resins of vinyl chloride and compounded materials. The method is based on sample dissolution and headspace gas chromatography. Concentrations of vinyl chloride in the range 0,1 mg/kg to 3,0 mg/kg can be determined.

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 472, *Plastics — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 472 apply.

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

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Principle

The level of vinyl chloride monomer is determined by headspace gas chromatography of the polymer test sample dissolved or swollen in *N,N'*-dimethylacetamide.

5 Sampling

A concentration gradient can form in stored resin samples due to the volatility of vinyl chloride. Cooling of the sample prior to sampling is advisable but condensation of humidity shall be avoided. Sample preparation shall be carried out as quickly as possible to minimize losses of residual monomer. When exchanging samples between laboratories or when storage is necessary, samples should be sealed in completely-filled glass bottles or vials (e.g. 6.5, 6.6).

6 Apparatus

Standard laboratory apparatus and the following:

6.1 Gas chromatograph (GC), fitted with an automatic static headspace sampler.

6.2 Gas chromatographic detector.

Any detector suitable for recording monomer vinyl chloride may be used.

6.3 Gas-chromatographic column.

The signal obtained with a solution containing 0,01 mg of vinyl chloride per litre shall be at least three times that of the baseline noise. The limit of detection of the method is 0,1 mg/kg vinyl chloride in test samples. Examples of suitable columns are described in Annex A, Table A.1.

6.4 Data-processing system, for data acquisition and evaluation of GC runs.

6.5 Glass bottles, capacity 30 ml, with polytetrafluoroethylene (PTFE) faced silicone septa and aluminium caps.

6.6 Glass vials, capacity 22,5 ml, with polytetrafluoroethylene (PTFE) faced silicone septa and aluminium caps.

6.7 Crimping and decapping tools, for sealing and uncapping the vials.

6.8 Glass pipettes, capacity 25 ml and 10 ml.

6.9 Microsyringes, capacity 500 µl and 100 µl.

6.10 Gastight glass syringe, capacity 10 ml, with lock valve.

6.11 Analytical balance, capable of weighing to 0,1 mg.

7 Reagents and materials

All reagents shall be of recognized analytical grade.

WARNING — Vinyl chloride is a hazardous substance which is a gas at ambient temperature. The preparation of solutions should therefore be carried out only under a well-ventilated fume hood.

7.1 Vinyl chloride, of purity greater than 99,5 %. The vinyl chloride gas cylinder shall be fitted with a syringe adapter.

7.2 *N,N′*-dimethylacetamide, density ρ = 0,937 2 g/ml[1]. The solvent shall not contain any impurity with the same chromatographic retention time as vinyl chloride under the conditions of the test.

WARNING — *N,N′*-dimethylacetamide is also a hazardous substance.

7.3 Detector gases and carrier gas: High-purity gases shall be used to achieve the required low limits of quantification.

7.4 Vinyl chloride, standard solution, with a vinyl chloride concentration of approximately 1 600 mg/l.

To a 30 ml glass bottle (6.5), add, using a glass pipette (6.8), 25 ml of *N,N′*-dimethylacetamide (7.2) and cap the bottle with a PTFE-lined silicone septum. Weigh (to 0,1 mg) the bottle containing the *N,N′*-dimethylacetamide. Introduce 10 ml of vinyl chloride gas through the septum into the *N,N′*-dimethylacetamide, using a pre-flushed 10 ml gastight syringe (6.10) and holding the end of the

syringe needle below the surface of the liquid. Avoid the contents of the bottle becoming contaminated by air. Identify this solution as solution A.

Repeat the procedure with a second 30 ml glass bottle and identify the resultant solution as solution B.

Leave both bottles for 2 h at room temperature to allow complete adsorption of the vinyl chloride. Reweigh to the nearest 0,1 mg to determine the mass of monomer which has been added. The mass of vinyl chloride in each standard solution will be about 40 mg, depending on cylinder pressure. Record the concentration of vinyl chloride in solutions A and B in milligrams per litre.

Store the solutions at a temperature of (7 ± 3) °C.

7.5 Vinyl chloride, working calibrant stock solutions, with a vinyl chloride concentration of approximately 32 mg/l.

To a 30 ml glass bottle, add, using a glass pipette, 25 ml of *N,N'*-dimethylacetamide (7.2) and seal with a PTFE-lined silicone septum and cap. Transfer 500 µl of solution A through the septum into the bottle using a suitable syringe.

Repeat for solution B and label the two diluted calibrant solutions as solution C and solution D.

Record the concentration of vinyl chloride in the working calibrant stock solutions in milligrams per litre.

7.6 Vinyl chloride calibration solutions, with vinyl chloride concentrations between 0 mg/l and approximately 0,3 mg/l.

Take seven 22,5 ml headspace vials (6.6) and add, using a glass pipette, 10 ml of *N,N'*-dimethylacetamide (7.2) to each. Using a 100 µl syringe, transfer 0 µl, 20 µl, 40 µl, 50 µl, 60 µl, 80 µl and 100 µl of solution C into the individual vials and seal with silicone/PTFE septa and caps. Take two more 22,5 ml headspace vials and add 10 ml of *N,N'*-dimethylacetamide. To these add 20 µl of solution D (giving a final concentration of 0,06 mg/l) and seal with a septum and cap. These last two solutions are used as check solutions.

8 Procedure

8.1 Preparation of test solutions

Weigh 1 g of sample (to 0,1 mg) into a 22,5 ml headspace vial (cut compounded materials into small pieces) and add 10 ml of dimethylacetamide. Seal with a silicone/PTFE septum and then cap the vial. Repeat this to produce triplicate test solutions for each sample.

8.2 Gas chromatography

Depending on the type of gas chromatograph and column used for the determination, establish the appropriate GC and detector parameters.

NOTE For guidance, the transfer line temperature and column oven temperature profile established for a GC equipped with column 2 described in Annex A are:

— Transfer line temperature: 150 °C.

— Column oven temperature profile: Isothermal at 80 °C for 2 min, from 80 °C to 170 °C at 5 °C/min, then from 170 °C to 230 °C at 20 °C/min. Under these conditions, vinyl chloride elutes at 8,4 min.

8.3 Determination

Transfer the test solutions, calibrant solutions and two check solutions to the static headspace sampler. Equilibrate them at 70 °C for 1 h prior to analysis.

Suggested operating parameters for the headspace sampler are:

— needle temperature: 150 °C;

— pressurizing time: 1,0 min;

— injection time: 0,1 min;

— withdrawal time: 0,5 min.

8.4 Preparation of the calibration graph

Plot a graph of the vinyl chloride contents of the calibration solutions, in milligrams per litre, against the corresponding peak areas.

9 Calculation

Determine the vinyl chloride content, in milligrams per litre, of the three test solutions and two check solutions from the calibration graph.

The vinyl chloride content of the sample, expressed in milligrams per kilogram of resin, is given by Formula (1):

$$c_m = c_V \cdot 10 \quad (1)$$

where

c_m is the vinyl chloride content, in milligram per kilogram of the resin, of the test sample based on the mass of sample and volume of solvent as specified in 8.1;

c_V is the vinyl chloride content, in milligrams per litre of the solution, of the test solution, determined from the calibration graph.

Report the results for each of the three test solutions individually, as well as their arithmetic mean and the standard deviation from the mean, to the nearest 10^{-1} mg/kg.

In case of significant deviations of the results obtained for the check solutions (7.6), the test shall be repeated.

10 Precision

The precision of the method is not known at the date of publication.

11 Test report

The test report shall include the following information:

a) a reference to this document, including its year of publication, i.e. ISO 6401:2022;

b) all details necessary for complete identification of the material tested;

c) necessary details of the test apparatus, detector and column used as well as required test parameters;

d) the individual results for the test solutions, their arithmetic mean and the standard deviation;

e) the expected and measured vinyl chloride monomer content of the two check solutions;

f) any deviations from the procedure;

g) any unusual features observed;

h) the date of the test.

Annex A
(informative)

Suitable GC columns for the determination of vinyl chloride monomer

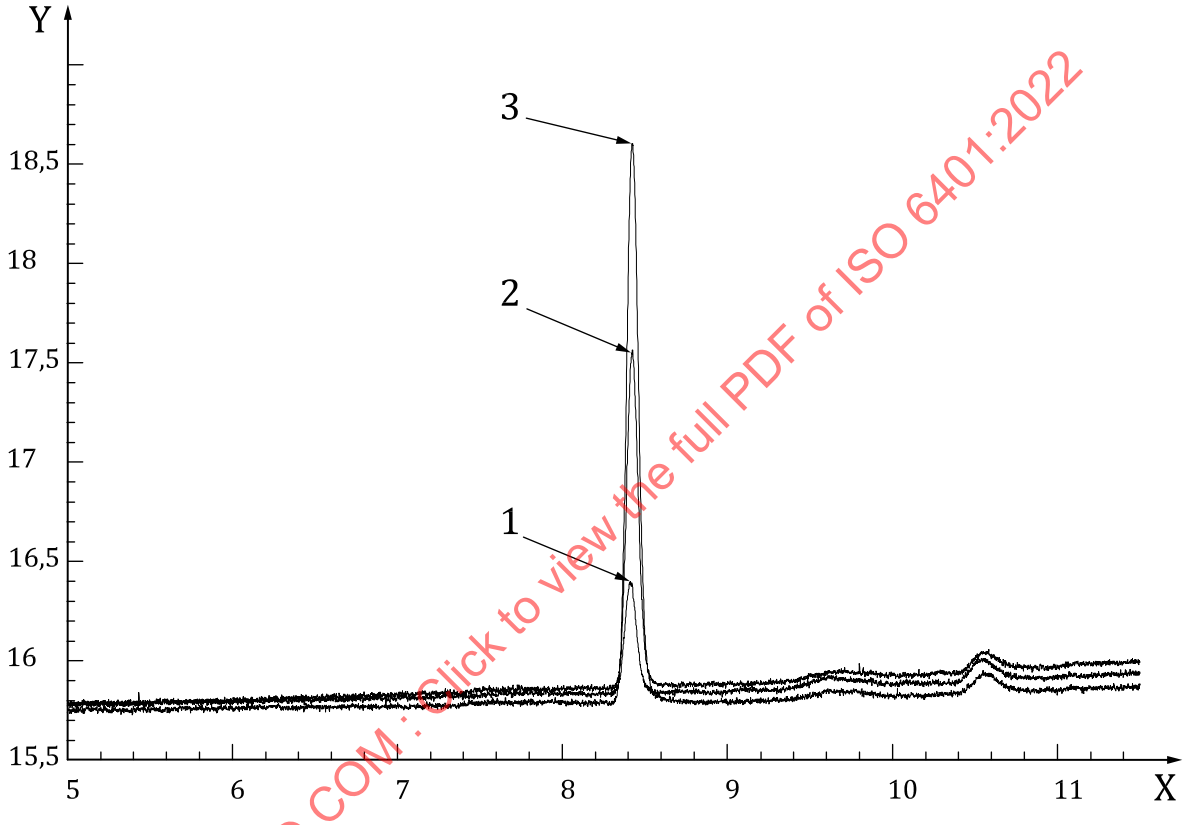
The PLOT (porous layer open tubular) columns described in Table A.1 have been found to be suitable for the determination.

Table A.1 — Suitable columns

Column	Length m	Diameter mm	Column type
1	15,00	0,53	Bonded polystyrene-divinylbenzene
2	30,00	0,53	Porous divinylbenzene homopolymer
An example of typical GC chromatograms obtained with column 2 is shown in Figure B.1.			

Annex B
(informative)

Typical responses for vinyl chloride monomer calibration solutions



Key

X elution time (min)
Y instrument response
1 0,06 mg/l vinyl chloride
2 0,19 mg/l vinyl chloride
3 0,31 mg/l vinyl chloride

Figure B.1 — Typical responses for vinyl chloride monomer calibration solutions in *N,N′*-dimethylacetamide using column 2 described in Annex A