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Plastics/rubber — Determination of residual monomers and other organic components by capillary-column gas chromatography —

Part 1: Direct liquid injection method

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO 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).

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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 9, *Thermoplastic materials*.

This second edition cancels and replaces the first edition (ISO 13741-1:1998), which has been technically revised.

The main changes are as follows:

— the title has been modified to 3 elements from 4 elements;

— part of the Scope (1.3) has been removed;

— Clause 3, Terms and definitions, has been added and subsequent clauses have been renumbered;

— Formulae (1) and (2) have been numbered.

A list of all parts in the ISO 13741-1 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.

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Introduction

The requirements imposed today by authorities include the assessment of the content of residual monomers and organic saturated volatiles, for health and environmental reasons sometimes down to minute traces. Former standards for measurement of residual volatiles based on distillation linked with titration cannot cope with such exigences.

This document presents an advanced method for the determination, by gas chromatography, of residual monomers and other organic components in polymer dispersions and lattices. It provides a method that is in line with present-day requirements for analytical methods, and is intended for use instead of ISO 3899, where precise measurements of volatile-matter content are needed, and expands their scope to include other volatile organic components.

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Plastics/rubber — Determination of residual monomers and other organic components by capillary-column gas chromatography —

Part 1:
Direct liquid injection method

WARNING — This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this document to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

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1 Scope

1.1 This document specifies a method for the determination of residual monomers and other (saturated) organic components in aqueous polymer dispersions and latices as well as in related products. It makes use of capillary-column gas chromatography with direct injection of the liquid sample.

1.2 Residual monomers and saturated volatiles that have been successfully determined by this method include acrylic and methacrylic esters, acrylonitrile, butadiene, styrene, vinyl acetate, vinyl chloride as well as by-products such as acetaldehyde and ethylbenzene.

2 Normative reference

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

3 Terms and definitions

No terms and definitions are listed in this document.

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

A test sample is diluted with water containing an internal standard and injected onto the liner of a gas chromatograph with a capillary column, a flame ionization detector and a linear temperature programming capability.

Butadiene can be co-eluted with cis-2-butene. Butyl acrylate and dibutyl ether shall be separated with DB5 column.

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5 Reagents

Unless otherwise stated, use only reagents of recognized analytical grade and only grade 1 water as defined in ISO 3696.

5.1 Carrier gas, Nitrogen, helium or hydrogen of 999,95 ml/l (or higher) purity. Hydrogen shall be used with a safety care.

5.2 Propionitrile, 990 g/kg purity, for use as internal standard.

Propionitrile has been found to be a suitable internal standard, but other at least partly water-soluble organic compounds not found in the sample can be used as the internal standard, e.g. iso-butyl acetate or methyl iso-butyl ketone. The internal standard shall yield a clear chromatographic separation and shall not interfere with any component originally present in the sample.

5.3 Monomers and other organic compounds of interest, 990 g/kg purity, for comparison purposes.

5.4 Dimethylformamide (DMF).

5.5 Tetrahydrofuran (THF).

6 Apparatus

Ordinary laboratory equipment, plus the following.

6.1 Gas chromatograph, having an injection port designed for split operation, with a liner of at least 1 cm^3 volume, a flame-ionization detector (FID) and a linear temperature programming capability for the column.

6.2 Capillary column, of length 30 m and internal diameter 0,53 mm, 0,32 mm or 0,25 mm made of fused silica that is covered inside with a 1 m to 5 m thick film of a dimethylpolysiloxane.

6.3 Integrator or suitable recorder.

Recording or integration is made using a chromatography data system (DTS), such as Chromeleon™[1)].

6.4 Microsyringe, capacity 10 µl to 50 µl.

6.5 Analytical balance, accurate to 0,1 mg.

6.6 Volumetric flasks, capacity 50 ml and 1 000 ml.

7 Preparation of apparatus

7.1 Partly fill the insert liner with glass wool to retain solids during injection.

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1) Chromeleon™ is the trademark of a product. 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.

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7.2 Control the detector temperature so that it is constant to within 1 °C, without thermostat cycling which causes an uneven baseline.

Table 1 — Typical operating conditions[a]

Detector	flame ionization
Air flow rate	300 or 450 ml/min
Hydrogen flow rate	30 ml/min
Make-up gas flow rate	30 ml/min
Column	
Length	30 m
Inside diameter	0,25 mm, 0,32 mm or 0,53 mm
Film thickness	1 µm to 5 µm (dimethylpolysiloxane)
Carrier gas	nitrogen or helium
Flow rate	0,8 to1,2 ml/min or 4 ml/min
Purge rate	1 to 2 ml/min
Temperatures	
Injection port	150 °C to 200 °C [c]
Detector block	250 °C
Initial column temperature	50 °C
Hold time	5 min
Program rate	5 °C/min
Final column temperature	200 °C (or higher as needed)
Final hold time [b]	7 minutes (or longer)
Injection volume	1 µl
Split ratio	10:1 to 100:1

[a] It may be necessary to modify these conditions if separation problems are encountered or if other conditions are specified in the gas chromatograph manufacturer's instructions. For instance, a column with an inside diameter <0,53 mm may be more suitable: in this case, reduce the carrier gas flow rate to ca. 1 cm^3/min.

[b] After the final hold, heating to 300 °C or 320 °C is recommended to purge the column.

[c] Methyl methacrylate is not thermally stable above 175 °C

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8 Calibration

8.1 For reliable results, it is necessary to calibrate the instrument for each analysis with respect to sensitivity and retention time.

This is done by determining the response factors and retention times for each component expected to be present in the dispersion or the latex by injecting small amounts of the internal standard together with the individual components, or mixtures thereof, dissolved in a solvent (e.g. dimethylformamide or tetrahydrofuran).

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8.2 Weigh, to the nearest 0,1 mg, about 100 mg of propionitrile and 50 mg to 200 mg of the volatile of interest (three to four different amounts are recommended) into a 50 ml volumetric flask. Make up to the mark with dimethylformamide or tetrahydrofuran and mix well.

8.3 Inject a 1 ml aliquot of the solution prepared in 7.1 into the injection block and record the chromatogram. Use the same instrument conditions as for sample analysis.

The elution order for typically occurring volatiles is as follows:

a) acetaldehyde;

b) 1,3-butadiene;

c) acrylonitrile;

d) propionitrile;

e) vinyl acetate;

f) methyl acrylate;

g) n-butanol;

h) ethyl acrylate;

i) methyl methacrylate;

j) 4-vinylcyclohexene;

k) ethylbenzene;

l) n-butylacrylate;

m) styrene;

n) 2-ethylhexyl acrylate;

o) 4-phenylcyclohexene.

8.4 Measure the peak areas of the individual components and calculate the relative response factor R_f for each component by Formula (1):

$$R_f = \frac{A_S \times m_V^o}{A_V \times m_S^o} \quad (1)$$

where

R_f is the response factor for the volatile of interest relative to the internal standard;

A_S is the peak area of the internal standard (propionitrile);

A_V is the peak area of the volatile of interest;

m_S^o is the mass of the internal standard in the calibration mixture;

m_V^o is the mass of the volatile of interest in the calibration mixture.

8.5 Calculate the mean response factor for each volatile.

8.6 Repeat this calibration as needed.

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8.7 Typical response factors are:

— butadiene 6

— 4-vinylcyclohexene 0,6

— ethylbenzene 0,6

— n-butyl acrylate 0,95

— styrene 0,6

9 Procedure

9.1 Prepare a dilute solution of the internal standard by weighing, to the nearest 0,1 mg, about 250 mg of propionitrile into a 1 000 ml volumetric flask. Make up to the mark with water (grade 1). Shake gently. Calculate the mass fraction w_S of the internal standard in this solution, expressed in milligrams per kilogram.

Prepare a fresh solution each day the test method is carried out. Take care to minimize losses due to evaporation.

9.2 Weigh out, to the nearest 0,01 g, about 10 g (or a suitable fraction of 10 g) of the sample (m_d), and add 30 g (or the same fraction of 30 g as for the sample), also weighed to the nearest 0,01 g, of the internal standard solution prepared in 8.1 (m_S).

9.3 Inject approximately 1 ml of the sample solution prepared in 8.2 onto the insert liner of the gas chromatograph using the instrument conditions given in Table 1 or similar conditions. If needle blockage occurs during the injection, needle shall be washed out using an appropriate solvent.

9.4 Immediately after injection, clean the syringe with water (grade 1) and with a water-miscible solvent (for example tetrahydrofuran).

9.5 Clean or replace the insert liner after every 10 to 20 injections.

9.6 Measure the peak areas of the internal standard, A_S, and of the relevant volatiles, A_V.

10 Calculation

Calculate the mass fraction w_V, in milligrams per kilogram, of each volatile present in the polymer dispersion/latex by Formula (2):

$$w_V = \frac{A_V \times R_f \times w_S \times m_S}{A_S \times m_d} \quad (2)$$

where

w_S is the mass fraction, in milligrams per kilogram, of the internal standard in the solution prepared in 9.1;

A_V is the peak area of the volatile of interest;

A_S is the peak area of the internal standard;

m_S is the mass, in grams, of internal standard solution in the sample solution prepared in 9.2 (e.g. 30 g);

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m_d is the mass, in grams, of sample in the sample solution prepared in 9.2 (e.g. 10 g);

R_f is the response factor for the volatile of interest, determined in accordance with 8.4.

EXAMPLE 260 mg of propionitrile was made up to 1 000 g with water (w_S = 260 mg/kg). 10 g of polymer dispersion/latex (m_d = 10 g) was mixed with 30 g of internal standard solution (m_S = 30 g). The peak area of the propionitrile was 18 000 units and that of the volatile 24 000 units. The response factor was determined to be 0,8.

Then

$$w_V = \frac{24\ 000 \times 0{,}8 \times 260 \times 30}{18\ 000 \times 10}$$

A typical chromatogram is shown in Figure 1.

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