INTERNATIONAL STANDARD

ISO 13741-1

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Plastics/rubber — Polymer dispersions and rubber latices (natural and synthetic) — Determination of residual monomers and other organic components by capillary-column gas chromatography —

Part 1:
Direct liquid injection method

Plastiques/caoutchouc — Dispersions de polymères et latex de caoutchouc (naturel et synthétique) — Détermination des monomères résiduels et autres constituants organiques par chromatographie en phase gazeuse sur colonne capillaire —

Partie 1: Méthode d'injection liquide directe

Reference number
ISO 13741-1:1998(E)

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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 13741-1 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 9, *Thermoplastic materials*, in close collaboration with ISO/TC 45, *Rubber and rubber products.*

ISO 13741 consists of the following parts, under the general title *Plastics/rubber — Polymer dispersions and rubber latices (natural and synthetic) — Determination of residual monomers and other organic components by capillary-column gas chromatography*:

— *Part 1: Direct liquid injection method*

— *Part 2: Headspace method*

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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 part of ISO 13741 presents an advanced method for the determination, by gas chromatography, of residual monomers and other organic components in polymer dispersions and latices. This standard provides a method that is in line with present-day requirements for analytical methods and is intended for use instead of ISO 2008:1987, *Rubber latex, styrene-butadiene — Determination of volatile unsaturates,* and ISO 3899:1988, *Rubber — Nitrile latex — Determination of residual acrylonitrile content*, where precise measurements of volatile-matter content are needed, and expands their scope to include other volatile organic components.

Plastics/rubber — Polymer dispersions and rubber latices (natural and synthetic) — Determination of residual monomers and other organic components by capillary-column gas chromatography —

Part 1:
Direct liquid injection method

WARNING — This part of ISO 13741 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 part of ISO 13741 to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

1.1 This part of ISO 13741 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. Butadiene could be co-eluted with *cis*-2-butene.

1.3 Since the chromatograms obtained normally contain a series of peaks, it is only possible to determine the content of those volatiles for which response factors have been determined. For the identification of unknown peaks, auxiliary methods like mass spectroscopy or the use of a second GC column with a different polarity are advisable.

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this part of ISO 13741. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this part of ISO 13741 are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

3 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.

4 Reagents

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

4.1 Carrier gas: nitrogen or helium of 99,995 % (or higher) purity.

4.2 Propionitrile, 99 % 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 could 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.

4.3 Monomers and other organic compounds of interest, 99 % purity, for comparison purposes.

4.4 Dimethylformamide (DMF).

4.5 Tetrahydrofuran (THF).

5 Apparatus

Ordinary laboratory equipment, plus the following:

5.1 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.

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

5.3 Integrator or **suitable recorder.** The recorder shall have a full-scale deflection of 10 mV, a time to full-scale deflection of 2 s or less, and a maximum noise level of ± 0,03 %.

5.4 Microsyringe, capacity 10 µl to 50 µl.

NOTE — It has been found that 50 µl microsyringes are more reliable and stable than smaller syringes. The needle is not prone to clogging. However, small (10 µl) microsyringes could, in principle, also be used.

5.5 Analytical balance, accurate to 0,1 mg.

5.6 Volumetric flasks, capacity 50 cm^3 and 1 000 cm^3.

6 Preparation of apparatus

6.1 Partly fill the insert liner with a piece of stainless-steel gauze with 80 to 325 mesh (180 µm to 45 µm) to retain solids during injection.

6.2 Condition the column by attaching one end of the column to the inlet side of the apparatus, leaving the exit end of the column disconnected. This prevents contamination of the detector due to column bleed. Set the carrier gas flow rate to the value given in the instruction manual and purge the column at 220 °C for 1 h (or longer).

6.3 After conditioning, connect the exit end of the column to the detector and establish the operating conditions required to give the desired separation (for typical conditions, see table 1). Allow sufficient time for the apparatus to reach equilibrium as indicated by a stable baseline.

6.4 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[1)]

Detector	flame ionization
Air flow rate	240 cm^3/min
Hydrogen flow rate	30 cm^3/min
Make-up gas flow rate	30 cm^3/min
Column	
Length	30 m
Inside diameter	0,53 mm
Film thickness	1 µm to 5 µm (dimethylpolysiloxane)
Carrier gas	nitrogen or helium
Flow rate	4 cm^3/min
Purge rate	1 cm^3/min to 2 cm^3/min
Temperatures	
Injection port	150 °C to 200 °C
Detector block	250 °C
Initial column temperature	50 °C
Hold time	5 minutes
Programme rate	5 °C/min
Final column temperature	200 °C (or higher as needed)
Final hold time [2)]	7 minutes (or longer)
Injection volume	approx. 1 µl
Split ratio	10:1 to 100:1

1) 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.

2) After the final hold, heating to 300 °C or 320 °C is recommended to purge the column.

7 Calibration

7.1 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).

7.2 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 cm^3 volumetric flask. Make up to the mark with dimethylformamide or tetrahydrofuran and mix well.

7.3 Inject a 1 µl aliquot of the solution prepared in 7.1 onto the column and record the chromatogram. Use the same instrument conditions as for sample analysis.

The elution order for typically occurring volatiles is given below:

acetaldehyde
1,3-butadiene
acrylonitrile
propionitrile
vinyl acetate
methyl acrylate
n-butanol
ethyl acrylate
methyl methacrylate
4-vinylcyclohexene
ethylbenzene
n-butylacrylate
styrene
2-ethylhexyl acrylate
4-phenylcyclohexene

7.4 Measure the peak areas of the individual components and calculate the relative response factor R_f for each component as follows:

$$R_f = \frac{A_S \times m_V^\circ}{A_V \times m_S^\circ}$$

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° is the mass of the internal standard in the calibration mixture;

m_V° is the mass of the volatile of interest in the calibration mixture.

7.5 Calculate the mean response factor for each volatile.

7.6 Repeat this calibration as needed.

7.7 Typical response factors are:

butadiene	0,6
4-vinylcyclohexene	0,6
ethylbenzene	0,6
n-butyl acrylate	0,95
styrene	0,6

8 Procedure

8.1 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 cm^3 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.

8.2 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).

8.3 Inject approximately 1 µl 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.

NOTE — It is advisable to use a 50 µl syringe for the injection to avoid problems with clogging of the needle due to film formation.

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

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

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

9 Calculation

Calculate the mass fraction w_V, in milligrams per kilogram, of each volatile present in the polymer dispersion/latex as follows:

$$w_V = \frac{A_V \times R_f \times w_S \times m_S}{A_S \times m_d}$$

where

w_S is the mass fraction, in milligrams per kilogram, of the internal standard in the solution prepared in 8.1;

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 8.2 (e.g. 30 g);

m_d is the mass, in grams, of sample in the sample solution prepared in 8.2 (e.g. 10 g);

R_f is the response factor for the volatile of interest, determined in accordance with 7.4.

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

$$w_V = \frac{24\,000 \times 0{,}8 \times 260 \times 30}{18\,000 \times 10} = 832 \text{ mg/kg}$$

A typical chromatogram is shown in figure 1.

Report results which are lower than 10 mg/kg (the detection limit) as < 10 mg/kg.

10 Precision

Duplicates should agree to within 15 %.

Repeatability should be 30 %.

Reproducibility has yet to be established. A general indication cannot be given as the reproducibility depends on the nature and amount of the volatile concerned.

11 Test report

The test report shall include at least the following information:

a) a reference to this part of ISO 13741;

b) the results obtained, calculated in accordance with clause 9;

c) the operating conditions used, if different from those in table 1;

d) the date of the test.

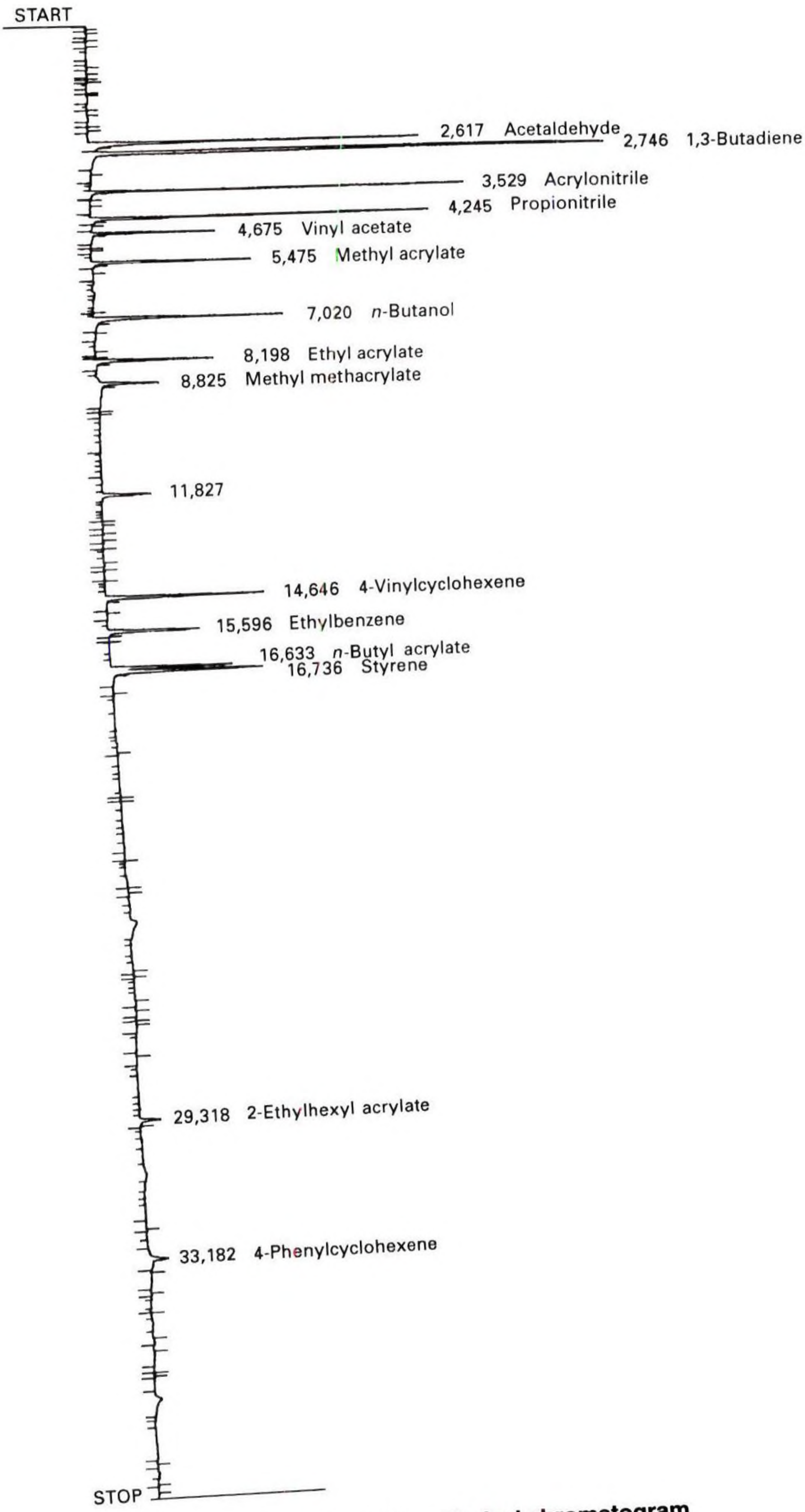

Figure 1 — Typical chromatogram