INTERNATIONAL STANDARD

ISO 13741-2

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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 2:

Headspace 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 2: Méthode de l'espace de tête

Reference number
ISO 13741-2:1998(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 13741-2 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 2:
Headspace 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 (unsaturated or saturated) organic components in aqueous polymer dispersions and latices as well as in related products. It makes use of capillary-column gas chromatography, the sample being introduced into the chromatograph in vapour form from a headspace vial.

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

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 suitable aliquot of the sample is diluted with water and with a water-miscible solvent containing an internal standard and a polymerization inhibitor. The mixture is introduced into a headspace vial and the vial sealed. The vial is allowed to come to thermal equilibrium and a measured quantity of the headspace vapours is introduced into a gas chromatograph with a capillary column, a flame ionization detector and a linear temperature programming capability. Sample introduction is achieved using commercially available automatic equipment.

4 Reagents

Unless otherwise stated, use only reagents of recognized analytical grade (purity > 99 %) and only grade 1 water as defined in ISO 3696.

4.1 Carrier gas: helium or nitrogen.

4.2 Dioxane, for use as an internal standard.

Dioxane *is one of several suitable internal standards. Other organic compounds not found in the sample could also* be used (e.g. methyl iso-butyl ketone). The internal standard shall not co-elute with any of the compounds of interest. Its retention time shall lie within the range covered by the compounds of interest.

4.3 Monomers, > 99 % purity, for comparison purposes.

4.4 Dimethylacetamide or **dimethylformamide.**

4.5 2,6-Di-tert-butyl-4-methylphenol, for use as a polymerization inhibitor.

5 Apparatus

Ordinary laboratory equipment, plus the following:

5.1 Gas chromatograph, having an injection port designed for split operation, a flame ionization detector (FID) and a linear temperature programming capability for the column, and capable of sequentially sampling and analysing the headspace vapours contained in sealed headspace vials.

5.2 Capillary column, of length 30 m and internal diameter 0,25 mm, made of fused silica that is covered inside with a 1 µm thick film of a dimethylpolysiloxane.

5.3 ***Integrator.***

5.4 Autosampler vials, capacity approx. 20 cm^3, suitable for headspace chromatography.

5.5 Aluminium- or PTFE-coated septa and **aluminium caps,** for sealing the vials.

5.6 Cap crimper.

5.7 Analytical balance, accurate to 0,1 mg.

5.8 ***Magnetic stirrer*** *or* ***roller mixer.***

6 Preparation of apparatus

6.1 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).

6.2 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.

6.3 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
The hydrogen, air and make-up gas (e.g. nitrogen) flow rates shall be optimized in accordance with the advice of the FID manufacturer	
Column	
Length	30 m
Inside diameter	0,25 mm
Film thickness	1 µm (dimethylpolysiloxane)
Carrier gas	helium or nitrogen
Column pressure	0,7 MPa to 1,7 MPa
Split	25 cm^3/min
Temperatures	
Detector block	300 °C
Initial column temperature	50 °C
Hold time	5 min
Programme rate	5 °C/min
Final column temperature	260 °C
Final hold time	10 min
Injection time/volume	6 s in the case of pressure-programmed sampling 1 ml in the case of sample-loop technique

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 < 0,25 mm may be more suitable: in this case, reduce the carrier gas flow rate to ca. 1 cm^3/min.

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 analysing the headspace above a solution of an internal standard together with the individual components, or mixtures thereof, dissolved in a solvent (e.g. dimethylacetamide). Use the same instrument conditions as for sample analysis.

7.2 Mix 1 cm^3 of water with 2 cm^3 of internal standard solution (containing about 500 µg of dioxane per 1 cm^3 of dimethylacetamide) and a small volume (< 50 µl) of a mixture of the volatiles of interest in which the mass fractions of the volatiles of interest are in proportion to the mass fractions in the sample.

It is advisable to perform the calibration procedure at different concentration levels (three or four different concentrations are recommended).

7.3 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;

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.

7.4 Calculate the mean response factor for each volatile.

7.5 Repeat this calibration as needed.

7.6 Typical response factors are:

ethylbenzene	approx. 0,1
styrene	approx. 0,2
4-phenylcyclohexene	approx. 1

NOTE — R_f values depend strongly on the column used.

8 Procedure

8.1 Weigh, to the nearest 0,2 mg, about 0,5 g of the sample into a headspace vial. Add 1 cm^3 of water and 2 cm^3 of internal standard solution (containing about 500 µg of dioxane per 1 cm^3 of dimethylacetamide), cover with a septum and seal the vial so that it is pressuretight.

NOTE — Depending on the type of polymer and the analyte concerned, other high-boiling solvents that are miscible with water can also be used.

8.2 Homogenize the sample solution by stirring with a magnetic stirrer for 30 min to 4 h, depending on the composition, or by rolling the vials on a roller mixer for 24 h.

8.3 Heat the sample solution at 90 °C for 1 h to equilibrate the system and analyse the headspace vapours under the conditions given in clause 6.

8.4 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:

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

where

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 milligrams, of internal standard in the sample solution prepared in 8.1;

m_d is the mass, in kilograms, of sample in the sample solution prepared in 8.1;

R_f is the response factor for the volatile of interest, determined in accordance with 7.3.

NOTE — In special cases, calculation by the standard additions method or the multiple headspace extraction method may be more suitable.

Typical chromatograms are shown in figures 1 to 3.

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

10 Precision

The precision of this test method is not known because inter-laboratory data are not available.

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.

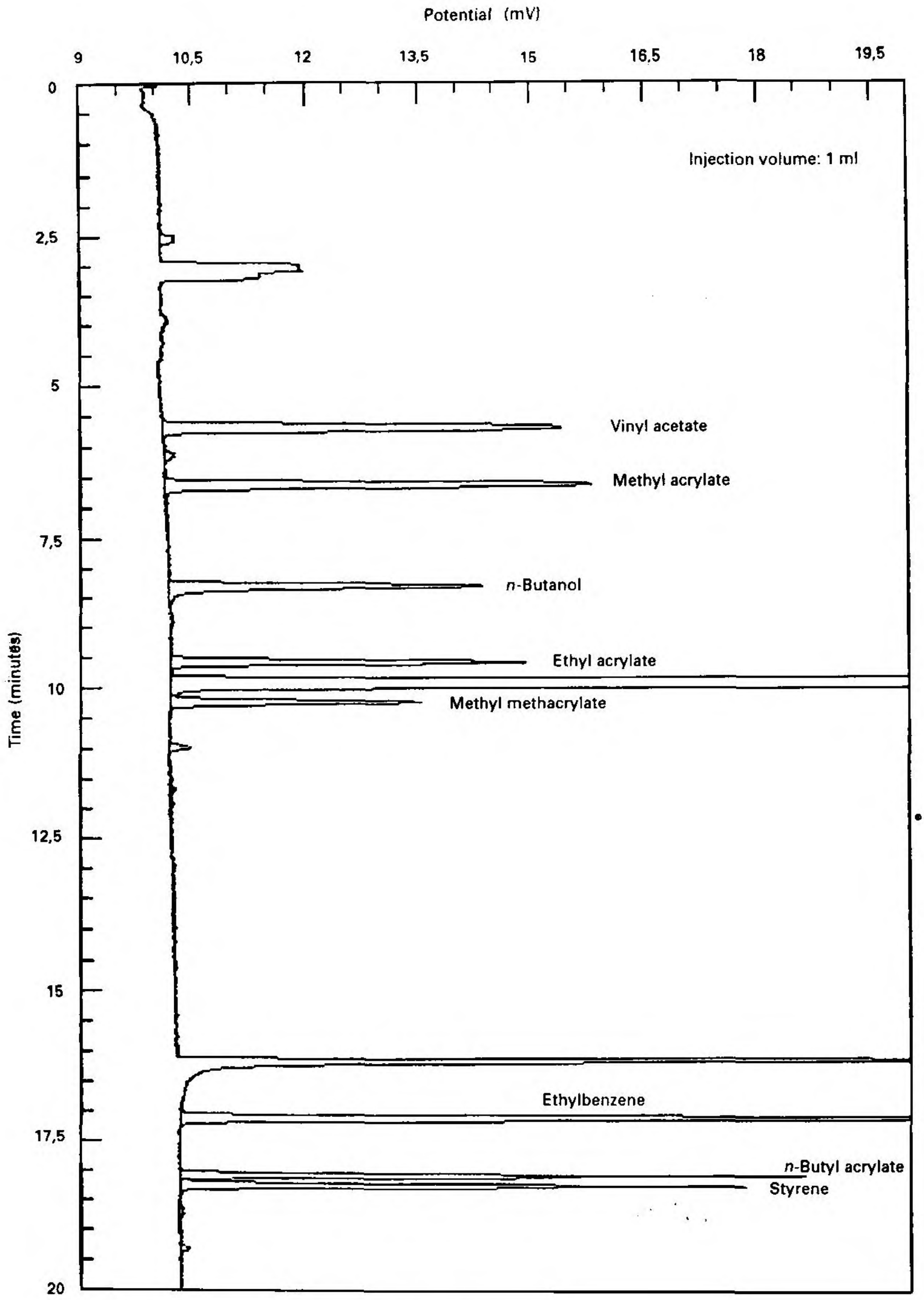
Potential (mV)
9
10,5
12
13,5
15
16,5
18
19,5
0
2,5
5
7,5
10
12,5
15
17,5
20
Time (minutes)
Injection volume: 1 ml
Vinyl acetate
Methyl acrylate
n-Butanol
Ethyl acrylate
Methyl methacrylate
Ethylbenzene
n-Butyl acrylate
Styrene

Figure 1

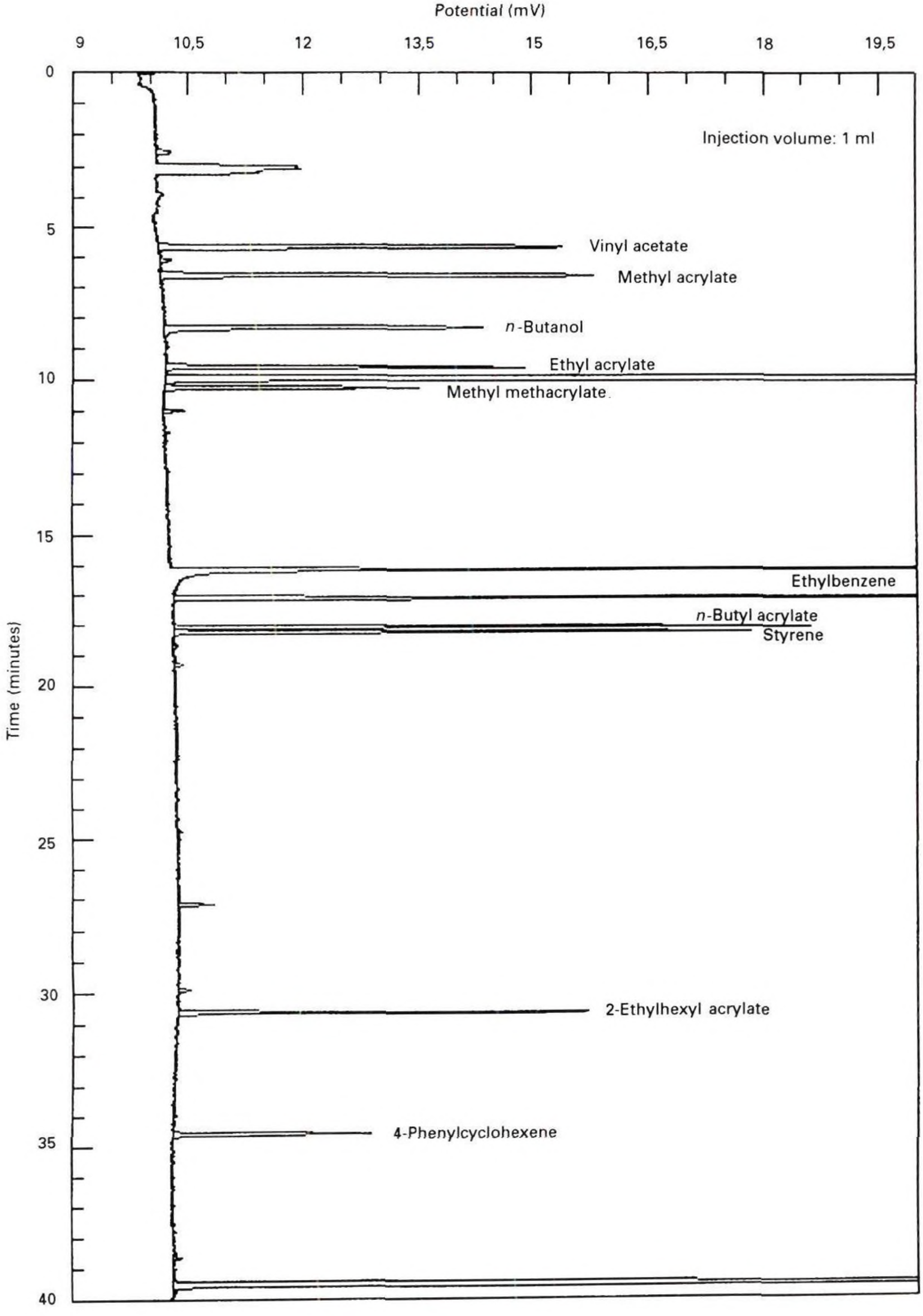
Potential (mV)
9
10,5
12
13,5
15
16,5
18
19,5
Time (minutes)
0
5
10
15
20
25
30
35
40
Injection volume: 1 ml
Vinyl acetate
Methyl acrylate
n-Butanol
Ethyl acrylate
Methyl methacrylate
Ethylbenzene
n-Butyl acrylate
Styrene
2-Ethylhexyl acrylate
4-Phenylcyclohexene

Figure 2

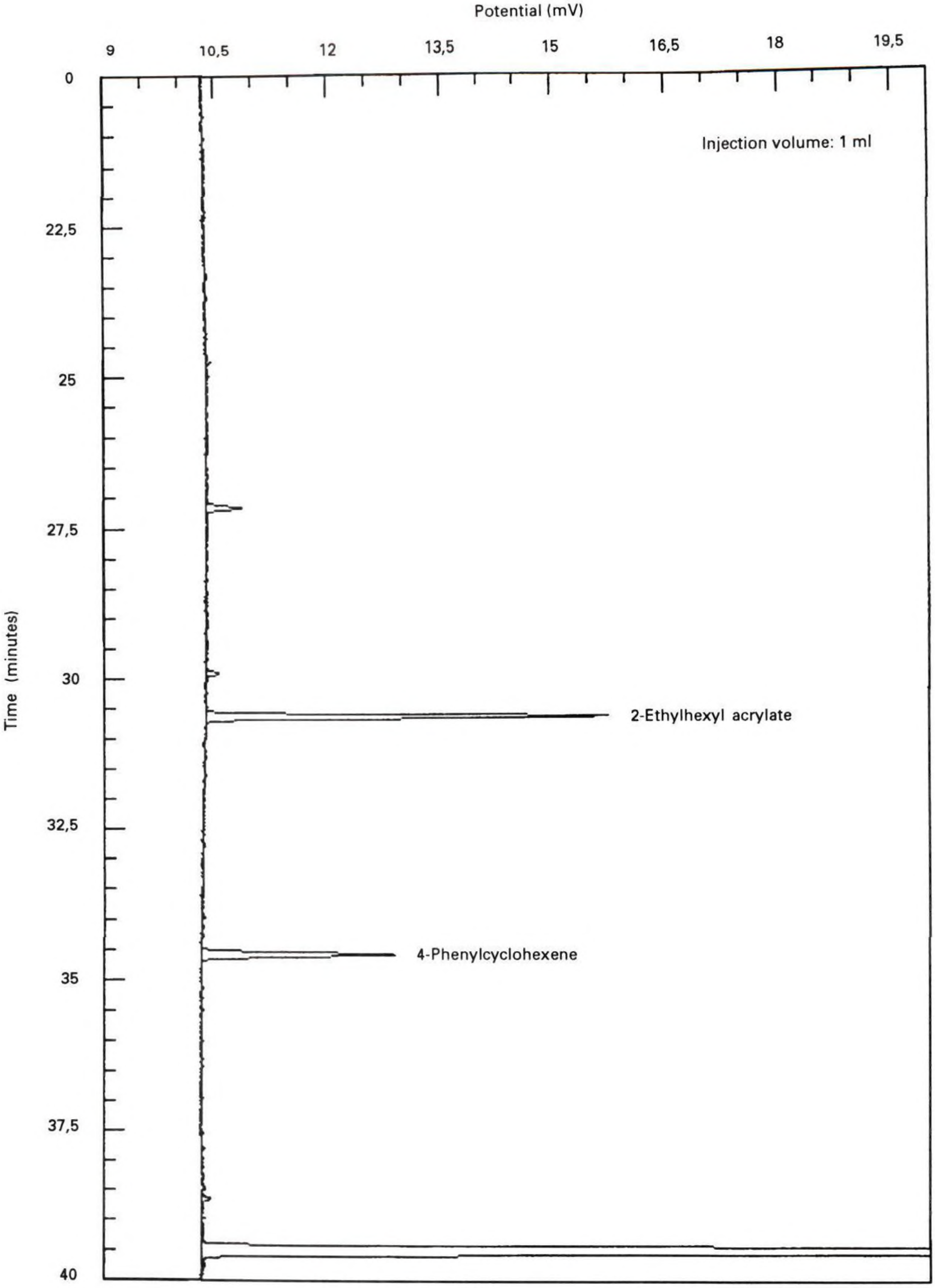
Potential (mV)
9
10,5
12
13,5
15
16,5
18
19,5
0
22,5
25
27,5
30
32,5
35
37,5
40
Time (minutes)
Injection volume: 1 ml
2-Ethylhexyl acrylate
4-Phenylcyclohexene

Figure 3