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International Standard ISO 7381

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Butadiene for industrial use — Determination of oligomers — Gas chromatographic method

Butadiène à usage industriel — Dosage des oligomères — Méthode par chromatographie en phase gazeuse

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 7381 was prepared by Technical Committee ISO/TC 47, *Chemistry*.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

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Butadiene for industrial use — Determination of oligomers — Gas chromatographic method

1 Scope and field of application

This International Standard specifies a gas chromatographic method for the determination of oligomers in butadiene for industrial use.

The method is applicable to butadiene having oligomer contents greater than 10 mg/kg.

The oligomers which may be present[1] are

- 4-vinyl cyclohexene;
- 1,3-cyclooctadiene;
- 1,5-cyclooctadiene.

2 References

ISO 6377, *Light olefins for industrial use — Determination of hydrocarbon impurities by gas chromatography — General considerations.*

ISO 8563, *Propylene and butadiene for industrial use — Sampling in liquid phase.*[2]

3 Principle

After obtaining a liquid sample at low temperature, injection of a liquid or gaseous test portion into a gas chromatography column.

Passage of the test portion through this column, allowing the separation of the oligomers, detection by flame ionization and comparison of the peaks obtained with those derived from an external standard.

4 Materials

4.1 Carrier gas

Nitrogen, helium or argon of purity > 99,9 %, containing no organic impurities or water.

4.2 Standard mixture

For each determination, prepare each time a standard mixture by dissolving an appropriate quantity, weighed to the nearest 0,1 mg, of 4-vinyl cyclohexene in a mixture of saturated hydrocarbons ranging from butane to heptane, so that the concentration of 4-vinyl cyclohexene corresponds to its expected concentration in the sample.

Transfer the mixture obtained to a vessel similar to that used for the sample and pressurize with an appropriate gas.

5 Apparatus

Ordinary laboratory apparatus, and

5.1 Dewar flask, transparent, permitting the butadiene to be maintained in the liquid state (see figure 1).

5.2 Test tube, for holding the liquid sample.

5.3 Chromatograph.

Use a gas chromatograph complying with the requirements specified below and which will yield a peak height of at least five times the background noise level for each oligomer at a concentration of 10 mg/kg.

5.3.1 Injection device.

a) Liquid sampling valve, allowing the successive introduction of liquid butadiene at its vapour pressure or at a greater pressure, and in adequate supply to satisfy the requirements of sensitivity and resolution according to the nature of the column (5.3.2) and of the detector (5.3.3).

b) Syringe, graduated in microlitres.

c) Stainless steel gas sampling valve with sample loop (if low oligomer contents presumed, see 3.2 in ISO 6377).

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1) With an appropriate choice of chromatographic conditions, other impurities such as acetonitrile, ethylbenzene or styrene (vinylbenzene) can also be determined by this method in recycled samples, which is illustrated in annex B.

2) At present at the stage of draft.

5.3.2 Column.

A number of columns which have been found suitable are described in annex A. Use one of these columns or any other column giving satisfactory separation or a combination of columns.

5.3.3 Detector, flame ionization type.

5.3.4 Recorder, having a response time, on the normal scale, of 2 s or less and a noise level less than 0,1 % on this scale.

5.3.5 Integrator.

6 Preparation of the sample

6.1 Use of an injection valve for liquid

The sample of butadiene, taken as indicated in ISO 8563, is maintained in the liquid state in the sampling cylinder.

6.2 Use of a syringe

Pour the liquid sample into the tube (5.2) inserted in the Dewar flask (5.1) cooled by solid carbon dioxide and acetone or methanol. Introduce the syringe [5.3.1b)] into the tube to cool it before use.

6.3 Use of an injection valve for gas

Carry out vaporization of the liquid sample as specified in ISO 6377, sub-clause 4.2.

7 Procedure

7.1 Preparation of the apparatus

Select a column (5.3.2) suitable for the determination to be performed and condition it by keeping it for at least 12 h at a temperature at least 20 °C higher than the operating temperature, using the carrier gas (4.1) at a flow rate equal to that to be used in the analysis.

Set up the column and carry out the adjustments necessary to produce the optimum operating conditions (see annex A). Wait a sufficient time for these conditions to become stable (as indicated by a stable base line).

7.2 Injection of the test portion

7.2.1 Use of an injection valve for liquid

Before introducing the sample into the injection valve for liquid [5.3.1a)], connect the sampling cylinder to earth by means of an equipotential clamp.

Inject through the column the required volume of the standard solution (4.2) so that the peaks will be as high as possible, taking into account the capability of the recorder (5.3.4).

Using the same quantity of test portion and under the same operating conditions, inject the sample through the column and record the peaks obtained.

7.2.2 Use of a Dewar flask and a syringe

Fill the syringe [5.3.1b)] to the appropriate volume and inject quickly into the chromatograph.

WARNING — The operator must wear gloves.

7.2.3 Use of an injection valve for gas

Proceed as indicated in ISO 6377, sub-clause 5.3.2.

7.3 Calibration

Inject the standard mixture (4.2) and record the peak for 4-vinyl cyclohexene.

7.4 Determination

Pass two test portions in succession through the chromatograph and record the peaks for each oligomer to be determined.

7.5 Examination of the chromatograms

7.5.1 Typical chromatograms

See annex B.

7.5.2 Measurement

Quantitative analysis is based on the measurement (A_i) of the height or of the area of the peak, by a method chosen by the user or from the reading of the integrator (5.3.5).

8 Expression of results

The concentration C_i of the oligomer i is given, in milligrams per kilogram, by the formula

$$C_E \times \frac{A_i}{A_E} \times \frac{E_i}{E_E}$$

where

C_E is the concentration, in milligrams per kilogram, of the standard material;

A_i is the measurement corresponding to the peak for oligomer i;

A_E is the measurement corresponding to the peak for the standard material;

E_i is the position of the attenuator during the measurement;

E_E is the position of the attenuator during the calibration.

NOTE — If the standard material is not identical to oligomer i, the concentration C_i of the oligomer i is given by the formula

$$C_E \times \frac{A_i}{A_E} \times \frac{E_i}{E_E} \times K_{E,i}$$

where $K_{E,i}$ is the coefficient of proportionality between the oligomer i in relation to the standard material.

If the detector is a flame ionization detector and the results are expressed in millilitres per cubic metre,

$$K_{E,i} = \frac{F_E}{F_i}$$

where

F_i is the number of carbon atoms in the molecule of the oligomer i;

F_E is the number of carbon atoms in the molecule of the standard material.

For each oligomer determined, calculate the mean of the two determinations and express the results in millilitres per cubic metre of product or in milligrams per kilogram of product.

9 Test report

The test report shall include the following information:

a) all information necessary for the complete identification of the sample (lot, date, time and duration of each sampling, etc.);

b) reference to this International Standard;

c) concentration of each oligomer determined;

d) nature of the oligomer and its concentration in the standard mixture;

e) statement of any experimental conditions which are regarded as optional:

- description of the column or combination of columns used,
- nature of the carrier gas,
- pressure, in bars*, of the carrier gas at the entrance to the column or in the first part of the column,
- flow rate of the carrier gas, in litres per hour, measured at standard atmospheric pressure,
- volume, in millilitres, measured at standard atmospheric pressure, of gas or liquid injected for each test,
- duration of the recording;

f) details of any unusual features noted during the determination;

g) details of any operations not included in this International Standard or in the International Standards to which reference is made, or regarded as optional.

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* 1 bar = 10^5 Pa

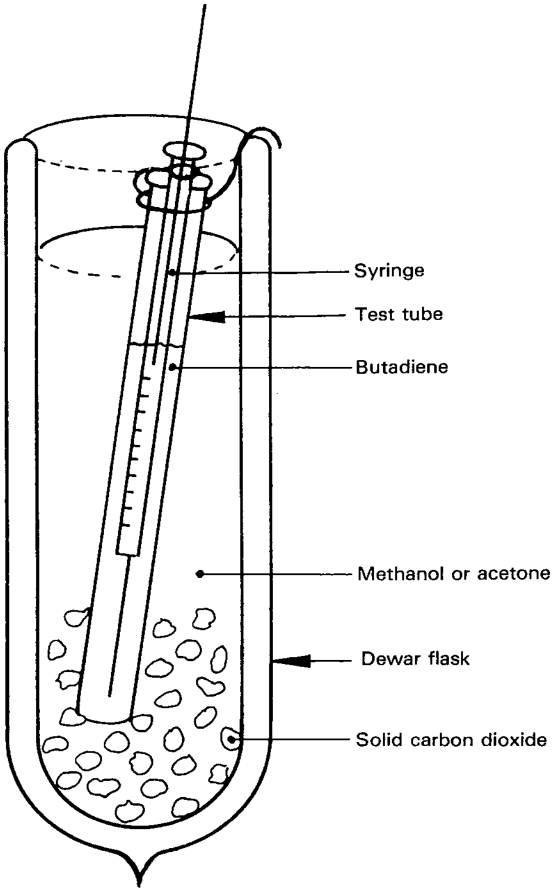

Figure 1 — Apparatus for storing the liquid butadiene before injection by syringe

Annex A

Columns and operating conditions which have been found suitable for the determination of oligomers in butadiene

(This annex forms an integral part of the Standard.)

Column	Carbowax 1540[1]	DC 200[2]	1,2,3-tris (2-cyanoethoxy) propane[3]
Length m	5	2	3
Internal diameter mm	2	2	2
Material	Stainless steel	Stainless steel	Stainless steel
Stationary phase	23 % Carbowax 1540	10 % DC 200	20 % 1,2,3-tris (2-cyanoethoxy) propane
Support	Chromosorb W-DMCS (60 to 80 ASTM mesh) (0,18 to 0,25 mm)	Chromosorb P (80 to 100 ASTM mesh) (0,15 to 0,18 mm)	Chromosorb W-AW-DMCS (80 to 100 ASTM mesh) (0,15 to 0,18 mm)
Temperature °C	140	85	80
Carrier gas	Nitrogen	Nitrogen	Nitrogen
Flow rate ml/min	25	20	30
Injection port temperature °C	175	175	175
Detector block temperature °C	200	200	200

[1] Carbowax 1540 = polyethyleneglycol 1540, $CH_3(CH_2)_{16}CO(OCH_2CH_2)_nOH$

[2] DC 200 = methylsilicone

[3] 1,2,3-Tris(2-cyanoethoxy) propane = 3,3′, 3′′-(1,2,3-propantriyl-trioxy)-tripropionitril, $NC\text{-}CH_2\text{-}CH_2\text{-}OCH(CH_2O\text{-}CH_2\text{-}CH_2\text{-}CN)_2$

Annex B

Typical chromatograms

(This annex forms an integral part of the Standard.)

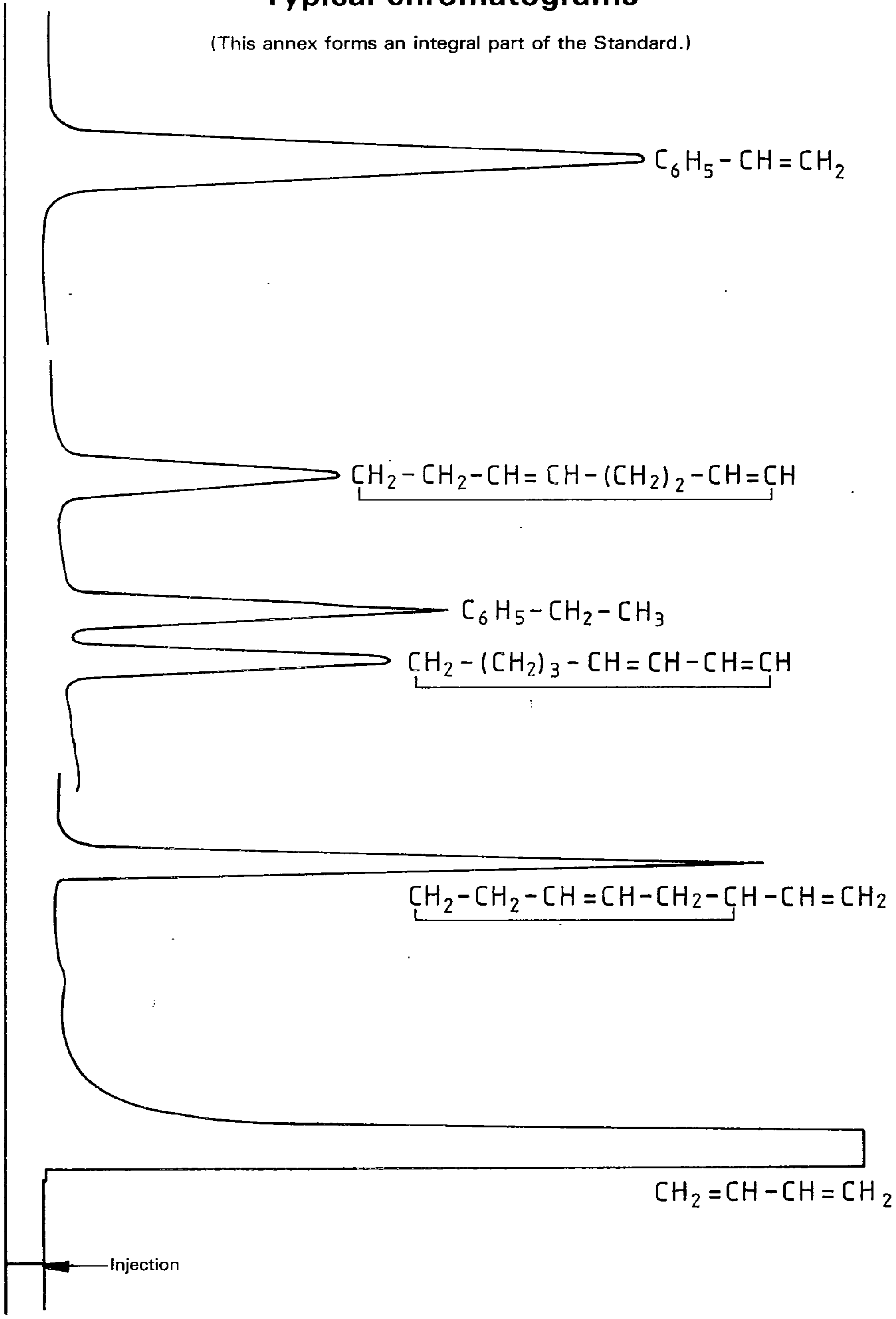

Figure 2 — Typical chromatogram from a Carbowax 1540 column (see annex A)

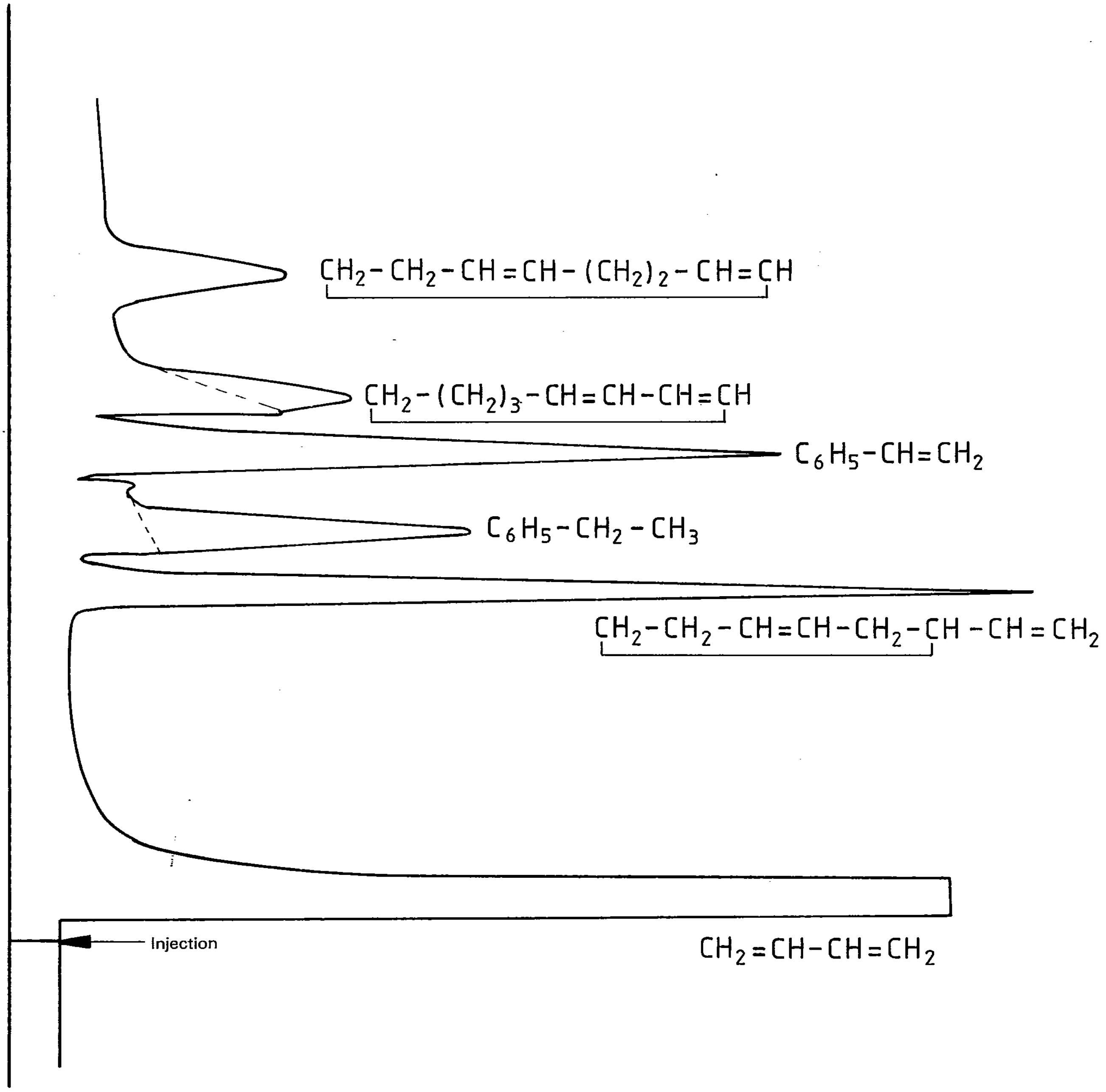

Figure 3 — Typical chromatogram from a DC 200 column (see annex A)

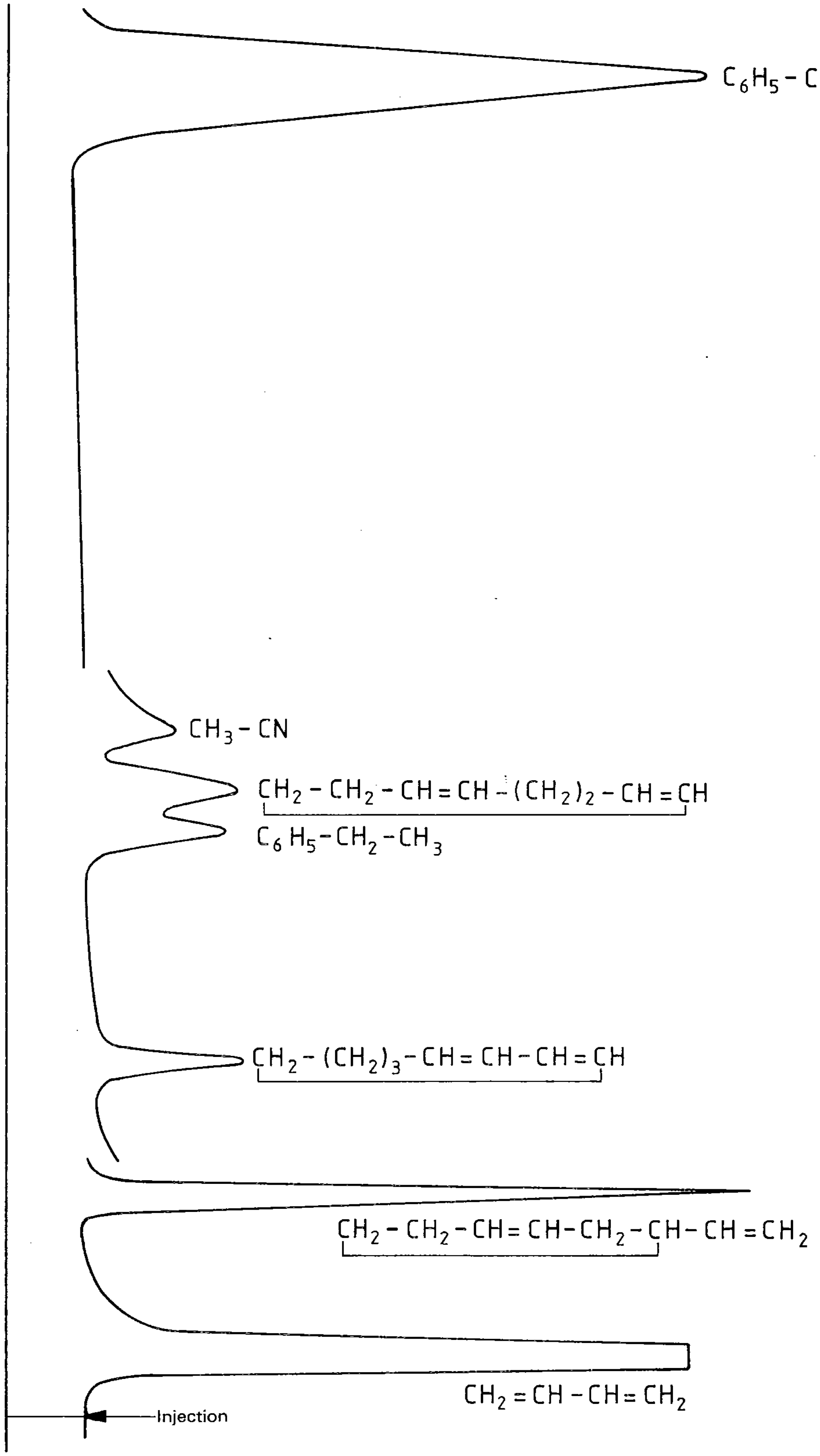

Figure 4 — Typical chromatogram from a 1,2,3-tris(2-cyanoethoxy) propane column (see annex A)