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

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

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International Standard ISO 8175 was prepared by Technical Committee ISO/TC 47, *Chemistry*.

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Propylene 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 propylene (propene) for industrial use.

The method is applicable to propylene having

propene dimers (hexenes) contents greater than 20 mg/kg and

propene trimers (nonenes) contents greater than 30 mg/kg.

NOTE — Propylene dimers are the main part of the so called "green oil" formed during partial hydrogenation to remove propadiene and propyne from propylene (about 8 %). Propylene dimers consist mainly of methylpentenes, 2,3-dimethylbutenes (about 25 %), hex-1-enes (about 12 %) and C_6-dienes (about 20 %).

2 References

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

ISO 8563, *Propylene and butadiene for industrial use — Sampling in liquid phase.* [1]

3 Principle

After obtaining a liquid sample at low temperature and vaporization, passage of a gaseous test portion through a chromatographic column which permits 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 or helium with purity better than 99,9 %, containing no organic impurities nor water.

4.2 Standard mixture

Prepare (or obtain) the following standard mixture:

propylene/hexene, the concentration corresponding to that expected in the sample.

If desired, a nonene may be added, the concentration being about 1/10 of the hexene concentration.

If necessary, use some *n*-decene, and determine its retention time, in order to estimate the retention times of the oligomers (see the figure).

The propylene used for the preparation of this mixture shall not contain detectable impurities having boiling temperatures higher than C_4 hydrocarbons.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Chromatograph.

Use a gas chromatograph complying with the requirements specified below and which will yield a peak height of at least five times the noise level for 20 mg hexene per kilogram (see ISO 6377).

5.1.1 Oven, permitting the column to be held at a uniform temperature within ±2 °C or better.

5.1.2 Injection system.

See ISO 6377, sub-clause 3.2.

5.1.3 Column.

The column and filling described below are given as an example. Any column, which completely separates the components to be determined, and which complies with the minimum requirements indicated in 5.1, may be used.

5.1.3.1 Tube

Tube forming the column shall be of stainless steel. The column shall be 3,5 m long with an external diameter of 3,3 mm and an internal diameter of 2 mm.

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[1] At present at the stage of draft.

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5.1.3.2 Support

A support based on calcined silica, acid-washed such as Chromosorb P/AW with particle size between 0,25 and 0,35 mm or Brick C-22 with the same particle size, shall be used.

After reducing the Brick C 22 to this particle size, wash it with 281 g/l potassium hydroxide solution, then with 182 g/l hydrochloric acid solution, and then with distilled water, and finally dry it for 24 h in an oven at about 180 °C.

5.1.3.3 Stationary phase

The stationary phase such as GE SE-52 (5 % of phenylmethylsilicone) or another nonpolar phase such as OV 101 (methylsilicone) shall be used.

The impregnation ratio shall be 13 % (13 g of stationary phase and 87 g of support). Carry out the impregnation by dissolving 13 g of the stationary phase in sufficient solvent [mixture of dichloromethane/toluene at 50% (*V*/*V*)] so that the whole of the solution completely covers the 87 g of support; evaporate the solvent by placing the mixture of support and solution in a rotary evaporator, heated to 100 °C under a current of nitrogen.

Sieve after impregnation, conserving the fraction 0,35 to 0,25 mm.

5.1.3.4 Method of filling and introduced mass

Fill the column in the vertical position by vibrating the holder while applying a vacuum to the lower end, closed by a porous plug. Use a mass of impregnated support of about 2,15 g/m, about 7,5 g total.

5.1.4 Detector, flame ionization type.

5.1.5 Recorder and **integrator.**

5.2 Gastight syringe

6 Sampling

Sample the propylene in accordance with ISO 8563 and vaporize it in accordance with 4.2 of ISO 6377.

The oligomers, also in the liquid phase, having a tendency to decant in the sampling cylinder, it is necessary to operate with small samples (50 to 100 ml) and to carry out the analysis immediately after sampling, following the procedure specified in ISO 6377, clause 4.

WARNING — During these operations, connect the sampling cylinders to earth by means of an equipotential clamp.

7 Procedure

7.1 Preparation of the apparatus

Condition the column (5.1.3) 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:

— injector port temperature : 250 °C;

— column temperature : preferably programmed, 70 °C initial temperature, rate 4 °C/min, up to 200 °C,

— carrier gas flow rate : chosen by the operator to obtain a suitable resolution, for example 30 ml helium/min,

— block detector temperature : 300 °C.

7.2 Injection of the test portion

Proceed as indicated in sub-clause 5.3.2 of ISO 6377 or alternatively with the gastight syringe (5.2).

7.3 Determination

Pass a portion of the standard mixture and then the test portion through the chromatograph.

The quantity injected, which shall be the same for the test portion and the standard mixture, will depend on the characteristics of the injection port in use.

Continue recording until the retention time of *n*-decene (for a guide see the table).

Continue recording the chromatogram of the standard mixture for the same effective time required for the recording for the test portion.

7.4 Examination of the chromatogram

7.4.1 Typical chromatogram

See the figure.

The propylene oligomers emerge as groups of peaks, separated from propylene, as well as from each other.

7.4.2 Retention time

The table gives the order of elution of the constituents and a guide to the relative retention times for temperature-programmed conditions.

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Table

Constituent	Relative retention time
Propane	1,00
Propylene (Propene)	1,00
Propene dimers (Hexenes)	1,18 to 2,35
Propene trimers (Nonenes)	2,35 to 6,47
n-Decene	7,71

7.4.3 Measurement

The quantitative measurement is based on the measurement of the peak area as by an integrator, since there are groups of fused peaks.

8 Expression of results

8.1 Method of calculation

The concentration C_i of dimer (trimer), expressed in milligrams per kilogram, is given by the formula

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

where

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

A_i is the total peak area of all dimers (trimers) obtained with the test portion;

A_E is the peak area of hexene obtained with the standard mixture;

NOTE — If th injected quantities of the sample and of the standard mixture are not equal, use the formula

$$C_E \times \frac{A_i}{A_E} \times \frac{Q_E}{Q_i}$$

where

Q_i is the quantity of sample injected;

Q_E is the quantity of standard mixture injected.

For each oligomer to be determined, calculate the mean of two determinations and express the results as milligrams per kilogram of the product.

8.2 Precision

8.2.1 Repeatability

The difference between the results obtained by the same operator, with the same apparatus, under the same operating conditions on the same material, shall not exceed more than one time in twenty times 4 % of the mean value.

8.3 Reproducibility

As it is impossible to circulate samples of compressed gases, it is not possible to carry out interlaboratory tests.

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 as required;

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 used, or, reference to the "Column specified in the International Standard",
- — 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 injected for each test,
- — duration of 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

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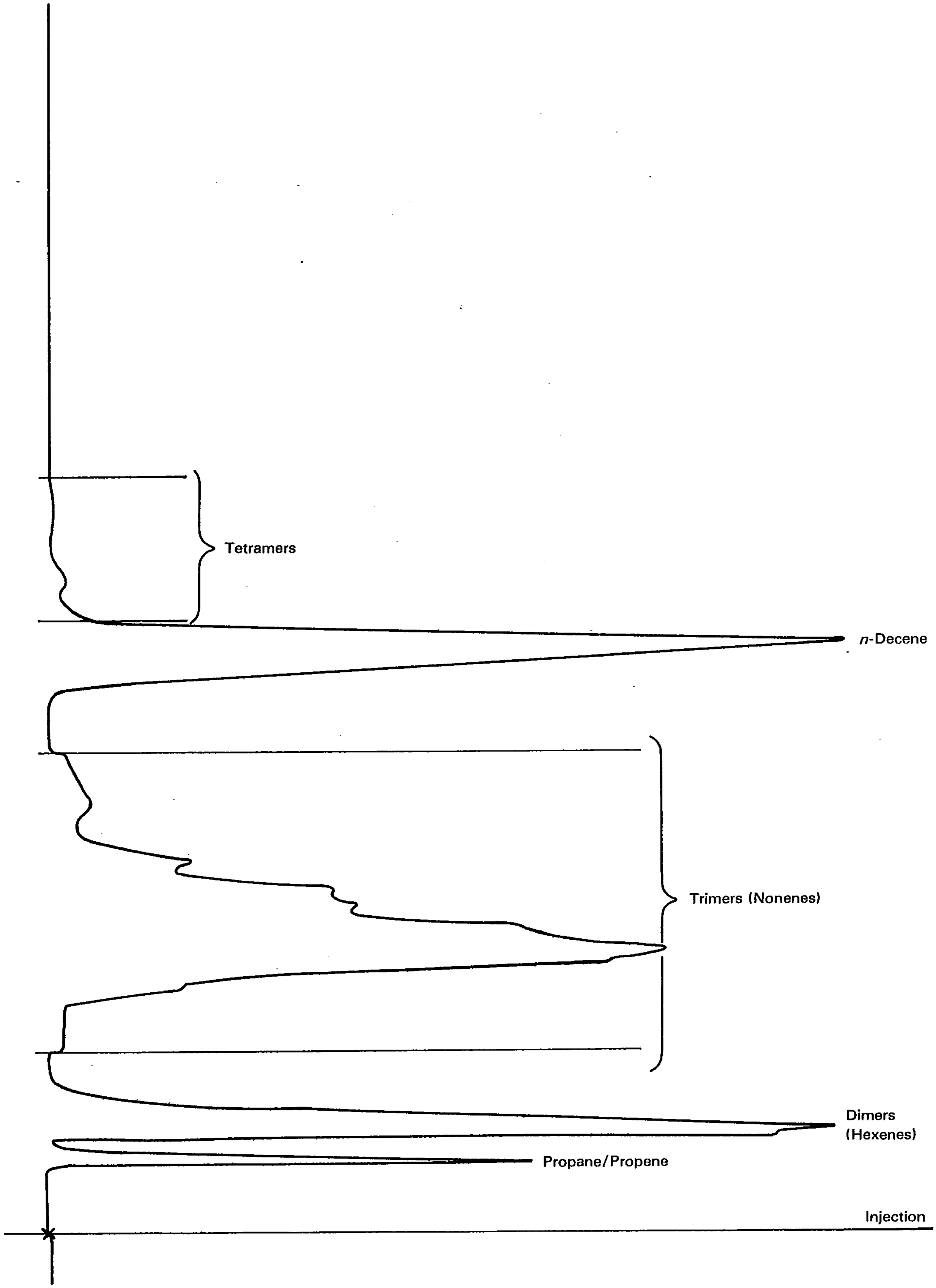

Figure — Typical chromatogram for a synthetic mixture

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