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Propylene for industrial use — Determination of hydrocarbon impurities — Gas chromatographic method

Propylène à usage industriel — Dosage des impuretés hydrocarbonées — 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.

International Standard ISO 6380 was developed by Technical Committee ISO/TC 47, *Chemistry*, and was circulated to the member bodies in October 1979.

It has been approved by the member bodies of the following countries :

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No member body expressed disapproval of the document.

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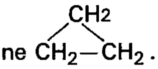
Propylene for industrial use — Determination of hydrocarbon impurities — Gas chromatographic method

1 Scope and field of application

This International Standard specifies a gas chromatographic method for the determination of hydrocarbon impurities in propylene for industrial use. It is applicable to the determination of the following impurities at levels greater than the values shown :

— methane (CH_4)	5 ml/m^3
— ethane ($CH_3—CH_3$)	5 ml/m^3
— ethylene (ethene) ($CH_2=CH_2$)	5 ml/m^3
— acetylene (ethyne) ($CH\equiv CH$)	5 ml/m^3
— propane ($CH_3—CH_2—CH_3$)	5 ml/m^3
— propadiene ($CH_2=C=CH_2$)	5 ml/m^3
— propyne ($CH_3—C\equiv CH$)	5 ml/m^3
— cyclopropane  $CH_2—CH_2$ (with CH2 bridging)	5 ml/m^3
— C_4 (saturated)	20 ml/m^3
— 1,3-butadiene ($CH_2=CH—CH=CH_2$)	10 ml/m^3
— butenes, total	20 ml/m^3

2 Reference

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

3 Principle

Passage of a gaseous test portion through a column which permits the separation of the impurities to be determined, detection by flame ionization and comparison of the peaks obtained with those derived from an external standard.

Two types of column are used, one for the determination of methane, ethane and acetylene (adsorption chromatography) and the other for the determination of the other impurities (gas/liquid partition chromatography).

The volumes and carrier gases selected shall permit separation of adjacent peaks of the impurities to be determined, as specified in sub-clause 5.1 of ISO 6377.

4 Materials

4.1 Carrier gas

Nitrogen, hydrogen or helium of the best available commercial quality, having water and oxygen contents each less than 5 ml/m^3.

4.2 Standards

Prepare (or obtain) the following standard mixtures :

- nitrogen/methane or nitrogen/ethane, for the determination of methane, ethane, ethylene and acetylene;
- nitrogen/propyne or nitrogen/propadiene, for the determination of these two relatively unstable impurities;
- nitrogen/propane, for the determination of the latter because of the many ranges of concentration of this impurity;
- nitrogen/*n*-butane, for the determination of the other impurities.

The nitrogen used for the preparation of these mixtures shall be at least 99,98 % pure and the water and oxygen contents shall each be less than 5 ml/m^3.

NOTE — Nitrogen may be replaced by helium or argon of the same purity.

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 at the concentration shown for each of the impurities listed in clause 1.

5.1.1 Oven, permitting the columns to be held at a uniform temperature below 30 °C and stable to ± 2 °C.

5.1.2 Injection device.

See ISO 6377, sub-clause 3.1.

5.1.3 Columns.

The combinations of columns and fillings described below are given as examples. Any column or combination of columns which will comply with the same minimum requirements for efficiency may be used.

5.1.3.1 Number

For adsorption chromatography, one column.

For partition chromatography, two columns in series differing only in length and the nature of the stationary phase.

5.1.3.2 Tube

For adsorption chromatography, the tube forming the column shall be of aluminium or stainless steel with a length of 2 m, an outside diameter of 6,4 mm and an internal diameter of approximately 4 mm.

For partition chromatography, the tubes forming the columns shall be of stainless steel. The first column, placed next to the injection port, shall be 6 m long, and the length of the second shall be 3 m. The outside diameter of each shall be 3,3 mm and the internal diameter shall be approximately 2 mm.

5.1.3.3 Support[1]

For adsorption chromatography, the filling shall be Spherosil XOB 075[2].

For partition chromatography, the support shall be Chromosorb P/AW or of brick C22, particle size 0,25 to 0,18 mm.

After reducing the brick C22 to this grain size, wash it with potassium hydroxide solution [c(KOH) ≈ 5 mol/l], then with hydrochloric acid solution [c(HCl) ≈ 5 mol/l], and then with distilled water, and finally dry it for 24 h in an oven at about 180 °C.

5.1.3.4 Stationary phase (for partition chromatography)

In the first column (6 m next to the injector), the stationary phase shall be di-*n*-butyl maleate; in the second (3 m), it shall be diethyl phthalate.

The impregnation ratio common to both stationary phases shall be 30 % (30 g of stationary phase and 70 g of support). Carry out the impregnation by dissolving 30 g of the stationary phase in sufficient *iso*-pentane or methylene chloride (chromatographic quality) so that the whole of the solution completely covers the 70 g support; evaporate the solvent by placing the whole in an unheated rotary evaporator under a current of nitrogen. Sieve after impregnation reserving the fraction 0,25 to 0,18 mm.

5.1.3.5 Method of filling and mass introduced

Fill the column in the vertical position by vibrating the holder while producing a vacuum through the lower end, closed by a porous plug. Use a mass of impregnated support of about 2,15 g/m for partition chromatography and about 5,5 g/m of Spherosil for adsorption chromatography.

5.1.4 Detector, flame ionization type.

5.1.5 Recording system : recorder, integrator or calculator, etc.

6 Preparation of sample

See ISO 6377, clause 4.

7 Procedure

7.1 Preparation of the apparatus

For both chromatographic methods, condition the column by keeping it for at least 12 h at the operating temperature, using a carrier gas 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 temperature : room temperature;
- column temperature : as preferred by the user, below 30 °C and stable within ± 2 °C;
- carrier gas flow rate : chosen by the user to obtain a suitable resolution;
- detector temperature : 100 °C minimum in order to avoid condensation of water vapour.

7.2 Injection of the test portion

See ISO 6377, clause 5.

7.3 Calibration

Inject, in succession, the standard mixtures (4.2) so as to display three peaks, at three different concentrations, for each impurity to be determined.

7.4 Determination

Pass two test portions, in succession, through the chromatograph.

The quantity injected, which shall be the same for the test portion and the standard mixtures, will depend on the design of the injection port used.

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[1] Information on proprietary products may be obtained from the Secretariat of ISO/TC 47/SC 14 (AFNOR) or from ISO Central Secretariat.

[2] Spherosil XOB 075 consists of pure silica in the form of spherical grains 100 to 200 µm in diameter.

Continue recording the adsorption chromatogram of the test portion until the appearance of the cyclopropane peak or until the end of the retention time of this substance (for guidance, see table 1).

Continue recording the partition chromatogram until the appearance of the 1,3-butadiene peak or until the end of the corresponding retention time (for guidance, see table 2).

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

7.5 Examination of the chromatogram

7.5.1 Typical chromatograms

See figures 1 and 2.

7.5.2 Retention time

Table 1 gives the order of elution, for the adsorption columns described in 5.1.3, of the constituents and a guide to the relative retention times. Table 2 gives the same information for the combination of partition chromatographic columns described in the same sub-clause.

Table 1

Methane	0,33
Ethane	0,49
Ethylene	0,77
Propane	1
Acetylene	1,74
Cyclopropane	2,19
Propylene	2,90

Table 2

Methane	0,31
Ethane and ethylene	0,63
Propane	0,92
Propylene	1
iso-Butane	1,43
Cyclopropane	1,67
Propadiene	1,79
n-Butane	1,94
Butene and *iso*-butene	2,26
Propyne	2,49
trans-2-Butene	2,74
cis-2-Butene	3,17
1,3-Butadiene	3,41

7.5.3 Calculation

See ISO 6377, clause 7.

8 Expression of results

8.1 Results

For each impurity determined, calculate the mean of two tests and express the results as millilitres per cubic metre of the product.

8.2 Repeatability

The difference between two results obtained by the same operator, with the same apparatus, under the same operating conditions on the same material, would in a long series of tests, in the normal and correct operation of the method, not exceed more than once in twenty times the values given in table 3.

8.3 Reproducibility

The difference between two single and independent results obtained by different operators in different laboratories on the same material, would in a long series of tests, in the normal and correct operation of the method, not exceed more than once in twenty times the values given in table 3.

Table 3 — Data for the determination of propadiene and propyne

Concentration ml/m^3	Repeatability ml/m^3	Reproducibility ml/m^3
10 to 20	2	5

9 Test report

See ISO 6377, clause 9.

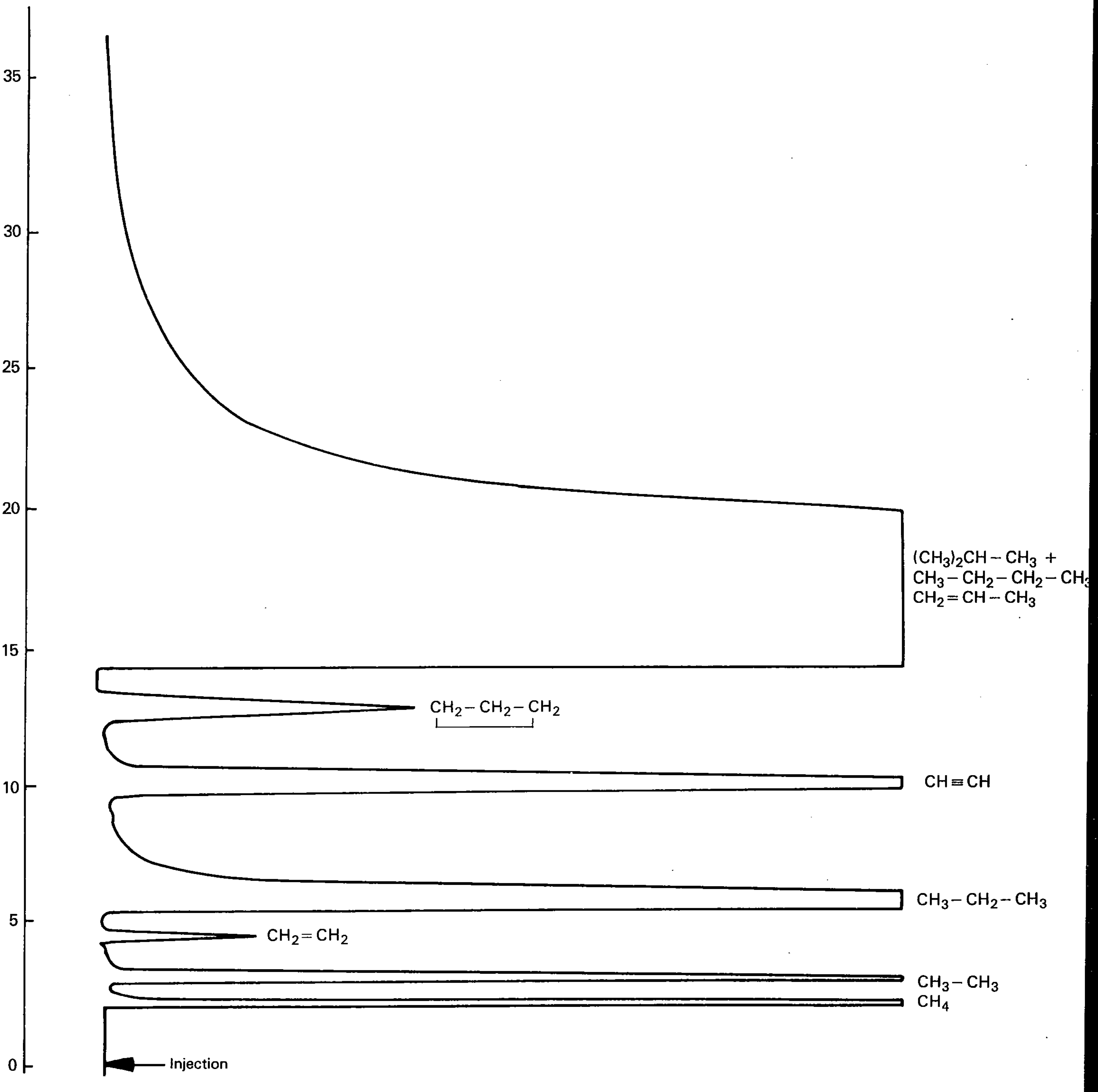

Figure 1 — Typical chromatogram from a Spherosil column

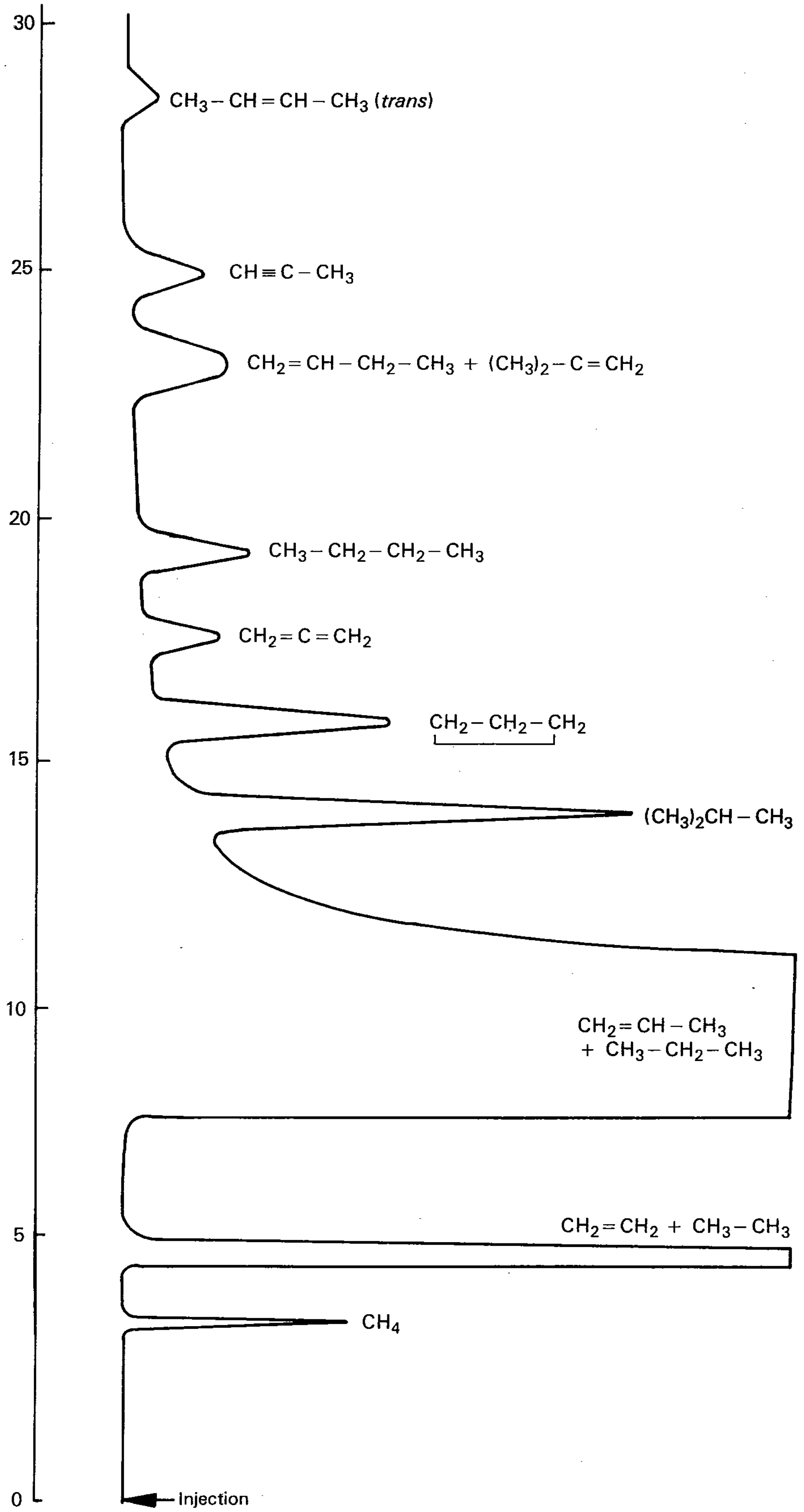

Figure 2 — Typical chromatogram from a di-*n*-butyl maleate and a diethyl phthalate column